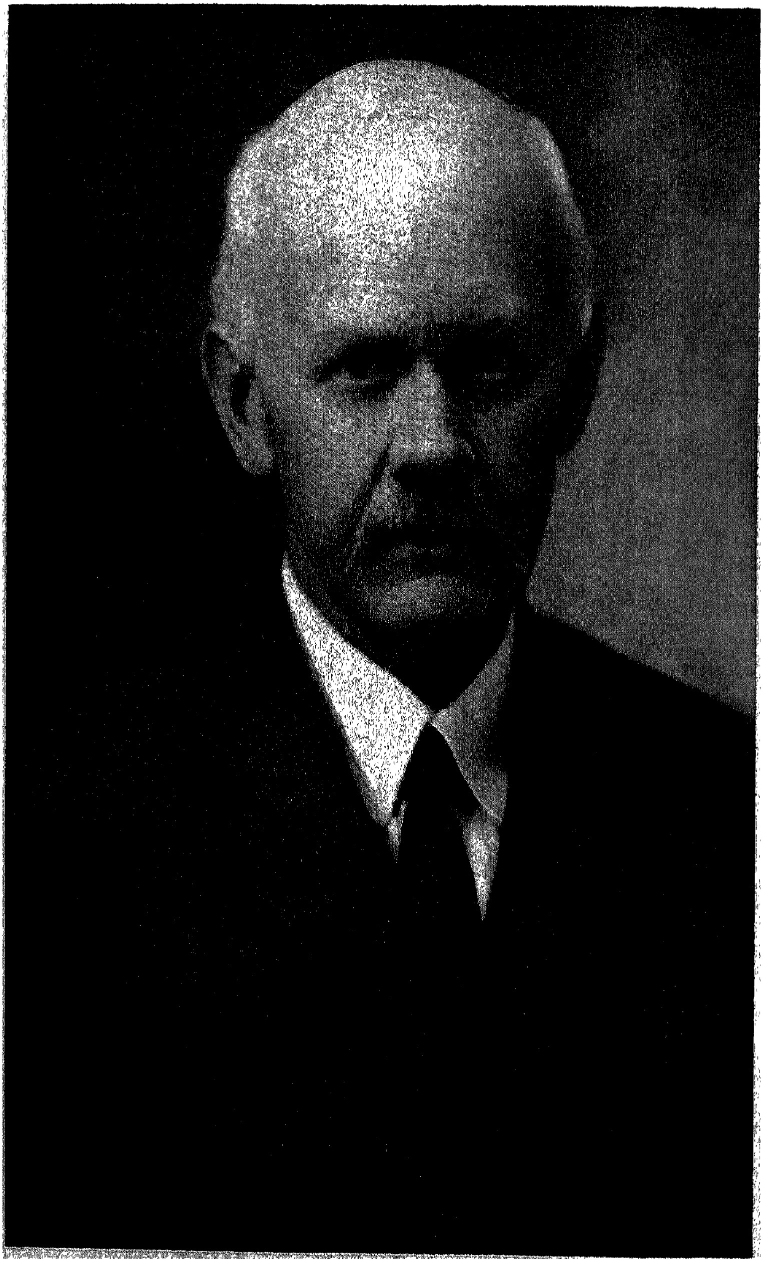

THE GEORGE FISHER BAKER
NON-RESIDENT LECTURESHIP IN CHEMISTRY
AT CORNELL UNIVERSITY

SOME PHYSICAL PROPERTIES OF

THE COVALENT LINK IN CHEMISTRY

BY

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TO ALL THOSE
YOUNG AND OLD
WHOSE FRIENDSHIP I ENJOYED
AT CORNELL UNIVERSITY

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PREFACE

This book is the basis of the lectures which I gave as George Fisher Baker Non-Resident Lecturer in Chemistry at Cornell University during the second semester of 1930-31.

I should like to express my warmest thanks to the staff of the Baker Laboratory for the cordial kindness with which they received me. To Professor L. M. Dennis I owe a special debt of gratitude for all his kindly help, and the trouble he took to make my visit easy and pleasant. To the members of the Cornell Branch of the Telluride Association I am more indebted than I can say for their hospitality and their friendship during the last half of my stay at Ithaca.

In the preparation of the book I have to thank many friends on both sides of the Atlantic for their assistance and advice, and especially Mr. E. J. Bowen, of University College Oxford, who has helped me with the spectroscopic methods and with the calculation of the heat data: Dr. L. E. Sutton, of Magdalen College Oxford, with whom I have discussed in detail the chapter on electrical dipole moments: Professor J. R. Johnson, of Cornell University, who has read the book in proof and made many useful suggestions: and Mr. L. G. Davy of Cornell University who has helped me in removing obscurities and in verifying references and calculations.

The book itself is an attempt to set out the methods of measurement of some of the more important properties of non-ionized links, and to discuss the results so far obtained. The subject is advancing so rapidly that even while the book was printing new methods have been evolved, and a mass of new data has accumulated. I have tried to include the more important researches bearing on these questions which have appeared up to the summer of 1932, and a few later ones of special interest. In such a subject no finality is possible; but it seemed to me that it is precisely while a subject is rapidly growing that a review of the methods and results is of service.

N. V. SIDGWICK

Lincoln College
Oxford
December 1932

INTRODUCTORY LECTURE

THE RELATION OF PHYSICS TO CHEMISTRY

I AM very grateful to Cornell University and to Professor Dennis for inviting me to join your staff as non-resident lecturer and for the kindness with which you have received me. It is a high honor to have one's name added to the distinguished list of the Baker lecturers. A lectureship of the kind founded by Mr. Baker is, I think, of real service both to the hosts and to the guests. Francis Bacon gives as one of the three chief conditions of scientific progress "conjunction of labor", the intercourse of scientific men, whereby, as he says, "the frailty of man may be supplied." With the progress of knowledge every branch of it becomes more specialized and yet at the same time more dependent on other branches, and the only way in which the workers in any laboratory can get a true sense of the values of the different kinds of chemical work which are being pursued all over the world is by intercourse with chemists from elsewhere. The benefit to the visitors is equally great, especially when it makes them acquainted with so admirable a laboratory and so distinguished a staff of chemists as you have here. I also appreciate greatly the opportunity of studying your methods of teaching and administration; the only way to find out how a university works is to join its staff and take part in its labors.

I have chosen "The Relation of Physics to Chemistry" as the subject of my introductory lecture, because it seems to me that there is none on which, in the present state of knowledge, it is more necessary that we should have clear views. While it is common to hear men deploring the increase of specialization, through which, they say, one scientific man can scarcely understand what another is doing, it is nevertheless true that the two great sciences of chemistry and physics have now reached a point at which they are attacking identical problems. The task which we as chemists have before us is no light one; neither chemists alone, nor physicists alone, can solve the problems which face us. We must make use of every assistance that we can get, and the most powerful is that of physics. But if we are to use this to the best advantage, we must understand clearly what it is, and in what ways it can help us.

It is a commonplace that all knowledge is one; its division into separate sciences is an unfortunate necessity, arising not so much from the subject-matter as from the limitations of human capacity. The field is so wide that no one can command the whole of it, and its students naturally break up into groups which concentrate on particular provinces and evolve particular methods for dealing with them. This means in practice that the various branches differ quite as much in the methods of attack as in the problems attacked. Among the sciences concerned with non-living matter, there are the three familiar divisions of mathematics, physics and chemistry. Mathematics deals with number, space and time, abstracted from all question of what it is that is numbered or what occupies the space; physics with the properties of matter, and primarily with those common to various forms of matter; chemistry with the properties of various forms of matter as related to their chemical composition. But these definitions, as you can see, are very imperfect; in fact, no exact boundaries can be laid down. Each science is crossing the frontiers of the next, and in recent years the interpenetration has been very rapid. Mathematics is becoming physicized; the word ether, which, when I was young, was used to distinguish real or physical from ideal or mathematical space, has almost disappeared, not because the concept of ether has been abandoned, but because we are more interested in real space than in imaginary spaces that might exist. Space and time are no longer independent entities, and for evidence of their interrelations we appeal not to *a priori* ideas, but to observations of the positions of stars and the wave-lengths of their light.

If the line separating mathematics from physics is blurred, that between physics and chemistry has vanished. Both sciences are now examining the same problems. It is true that they use different methods, but they apply them to the same materials. It is therefore of fundamental importance for us as chemists that the light which the physicists throw on our problems should illuminate them for us as well as for the physicists.

The distinction between different sciences depends on a very obvious fact, that the simpler the problem you are examining the more precise is the knowledge you can acquire of it—in philosophical language, the less the extension the greater the intension. The simplest problems of all are those of the mathematician. His materials—number, space and time—are uniform in behavior; he can isolate his problems from all outside interference. Hence he can state his results with the greatest certainty and accuracy, and carry his analysis to the greatest lengths. The physicist has a more complicated task; he has to take account of the differences in behavior of different forms of matter and of the small disturbances to which any actual system, however carefully isolated, is subject; and he must reckon with the imperfection of his measuring instruments. He is therefore often obliged to be content with approximations to the truth. The chemist is faced with still greater complications. While the physicist can restrict his inquiry to simple systems and to the materials which he finds most tractable, the chemist is compelled to extend his work to all forms of matter, or let us say in the first instance to all pure substances. Having this great mass of material to handle, his knowledge of its behavior is necessarily less detailed, less accurate, less deducible from first principles than that of the physicist, and in a still higher degree than that of the mathematician.

The series does not end with the chemist. The relation of the biologist to the chemist is like that of the chemist to the physicist, or of the physicist to the mathematician. He has to deal with structures elaborately built up of a variety of chemical substances, solid, colloidal and liquid; he can penetrate less deeply into these greater complexities.

The truth is that there is a scale of complexities from mathematics to biology—a scale not involving any gradation of moral or intellectual merit; whichever step the man of science stands on, he can rebuke those on one side of him for neglecting the complicating factors which affect all real phenomena, and those on the other for failing to see as deeply into the broader subjects of their inquiry as he himself does into his simpler problems. The accusation is equally true and equally pointless in each case. What we need to learn is not the weaknesses of our allies, which are very like our own, but their strength; we must discover in what ways they can be most serviceable to us.

To this end we may briefly consider how physics has helped chemistry in the past.

In one sense every chemical statement is also physical; it involves a physical background just as every quantitative statement of whatever kind involves a mathematical background. But apart from this general relation we can distinguish three periods in the history of chemistry as related to physics. From the earliest times when any real chemical theory existed—which for practical purposes means from the promulgation of the atomic theory at the beginning of the nineteenth century—down to about 1885, the chief service of physics to chemistry was the establishment of the existence, and the determination of the relative sizes, of molecules. Avogadro's hypothesis was essentially physical and although chemists as a whole (Faraday is a marked exception) disregarded it for nearly forty years they lost heavily by doing so, and it was only when Cannizzaro in the 50's demonstrated its importance to chemistry that a real knowledge of molecular composition—the necessary preliminary to a knowledge of structure—became possible. A little later, in 1874, came the definite physical proof of the soundness of the basis of the chemical molecular weights. These were all founded on the assumption that the molecule of hydrogen contained two atoms. Of this there was no positive evidence; the assumption was generally accepted because it was found to explain the facts; but it always remained possible that the hydrogen molecule contained four atoms, and that the number of atoms in all molecules was twice as great as was supposed. In 1874 Kundt and Warburg measured the ratio of the specific heats of mercury vapor at constant pressure and constant volume, and showed that its molecule could not possibly contain more than one atom. It was already known that there were twice as many atoms in a molecule of hydrogen as in a molecule of mercury, and so the final proof of the truth of the molecular theory was supplied.

For twenty-five years after Cannizzaro's paper the energies of chemists were largely devoted to developing the new theory of chemical structure, and to building up on this foundation the great edifice of organic chemistry. On the inorganic side the recognition of Avogadro's principle led to the assignment of the true atomic weights, and as soon as this had been effected the Periodic Classification necessarily and rapidly followed.

Then came in 1885 the second great application of physics, the introduction of thermodynamics into chemistry by van 't Hoff. The first investigations were indeed some thirty years earlier, and Willard Gibbs had already (1875–1878) published those far-reaching conclusions which were to prove so fruitful in chemistry and physics in later years. The main development, however, came from van 't Hoff. He applied the methods of thermodynamics, based on the general principles of energy, to a broad range of chemical phenomena. The most immediately important application was to the behavior of dilute solutions. He realized the great suitability of osmotic pressure for thermodynamic treatment. By means of an ideal engine precisely similar to the classical heat engine of Carnot, but with a solution separated from the solvent by a partition permeable to the solvent alone, he was able to establish, on the experimental basis of Henry's law of the variation of the solubility of a gas with the pressure, the relation between the molecular concentration and the osmotic pressure, and further the relation of this to more easily measurable properties of the solution, the lowering of the vapor pressure, the rise in the boiling point and the fall in the freezing point. He was also able to give a proof of the law of mass action, which had been established empirically some twenty years before. These discoveries initiated the subject of chemical thermodynamics, which has guided so much of the later developments of the science; and they ultimately led, in the hands of Nernst and others of van 't Hoff's successors, to the third law of thermodynamics and the chemical constants, and to those investigations of activity which are still in progress.

Perhaps the most immediately important result of this work was the rise of the theory of electrolytic dissociation. Van 't Hoff had shown what was the normal behavior of a solution. Experiment proved that while many solutions behaved as this theory required, those of salts in water did not; and their abnormality was always of the same kind: the salt appeared to form more molecules in the solution than corresponded to its formula. The explanation was given (1887) by Arrhenius, who argued that just as the abnormally low molecular weights indicated by the vapor densities of some gases were assumed and had been proved to be due to dissociation, so we must suppose that a salt dissociates in water; and since sodium chloride, for example, can dissociate only into its two atoms, and normal sodium and chlorine atoms cannot exist side by side in water, it must form charged ions of the two elements, a conclusion supported by the whole electrical behavior of the solution. The precise form which Arrhenius gave to the theory was, as we now realize, imperfect; but no one can doubt that by the recognition of a new kind of chemical change, and of a type of molecule peculiarly reactive, he gave an immense impulse to the development of chemistry.

The discoveries of van 't Hoff and Arrhenius were immediately followed by two events which are generally taken to mark the birth of physical chemistry as a primary division of chemistry, the call of Ostwald to Leipzig in 1887, and the foundation in the same year of the *Zeitschrift für physikalische Chemie*. Ostwald was in the very first rank as a teacher, if not quite as an investigator, and he was indefatigable in spreading the light of the new science, which yet was really no new science but, as Nernst says,[2] rather the union of two previously separated sciences. The work of the Leipzig school and their followers was largely along lines that had for many years been open for traffic, but had not been used; it consisted in making more precise the physical background which, as I said, underlies every chemical statement. The physical properties of chemical substances and their solutions, and the conditions of their reaction, were measured in detail, and the whole of chemistry assumed a more quantitative aspect. In organic chemistry the enormous variety of new compounds which it was found possible to prepare, and the wonderful success of the structural theory in classifying them, still gave its students plenty of occupation on the qualitative side; but here too the application of the new ideas to explain the behavior of organic compounds was undertaken by Hantzsch with the most illuminating results, and was extended later with great effect by Dimroth and others.

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[2] W. Nernst, *Theoretische Chemie* (1st. ed., *Stuttgart*, 1893).

The most important developments of the new science were, however, on the lines of thermodynamics and of the ionic theory. It is a remarkable sign of the predominance of the thermodynamic aspect at this time that Ostwald actually proposed to abandon the idea of atoms altogether; he conceived that he had provided an alternative explanation of the laws of chemical combination, involving no atomic theory but substituting the concept of "equivalent weight," whose meaning was not subject to discussion. By the irony of fate, this doctrine of Ostwald's was propounded exactly at the time when the physicists began their triumphant attack on the problem of the structure of the atom. Van 't Hoff had a truer insight into the fundamental problem of chemistry. He pointed out[3] that all natural phenomena may be looked at from two points of view, the thermodynamical and the molecular or atomistic. The nature of a thermodynamic argument is very peculiar. It is based on the fundamental principles of energy, which are as certain as anything we know in science. It lays down conditions of energy change to which a process must conform, granting certain external conditions, whatever its internal mechanism may be. This has the great advantage that, provided the deduction is carried out correctly, which in the simpler instances is not open to doubt, the conclusions are quite certain, and do not depend on the truth of any theory of the process. But for this reason it does not enable us to decide between two rival mechanisms, provided they can both give the same energy result. In particular, it takes no account of the time; the ideal processes of a thermodynamic cycle occur reversibly, *i.e.* with an infinitesimal driving force, and hence would in fact require an infinite time. So while thermodynamics tells us what the result will be, it does not tell us how we get there or how long the journey will take.

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[3] Van 't Hoff, *Lectures on Theoretical and Physical Chemistry* (London, 1899), Vol. I, p. 12.

Of the immense importance of thermodynamics as a calculus there can be no doubt; it lays down conditions to which every true theory must conform, and thus eliminates many false ones; and it has further the great practical use of enabling us to determine a property which it is difficult to measure directly, by observing some thermodynamically related property which is more accessible, as when we determine the osmotic pressure of a solution by observing the change of its freezing point, or the heat of dissociation of a gas from the change of density with temperature. But it answers only half our question; it does not tell us what the molecules are doing in a chemical process; as Ostwald's argument showed, it does not even involve the assumption that there are any molecules. For the proper development of chemistry, the thermodynamic side must be supplemented by the molecular-mechanical.

At the time of which I am speaking, the latter years of the nineteenth century, this second side of the matter could not be developed in great detail, because our knowledge of the molecule was so scanty. The relative masses of molecules and the number of atoms which they contained were known with accuracy; but for their absolute masses only the roughest approximations were available, and of the structure of the atoms and the mechanism which holds them together in the molecule, nothing was known at all. The discovery of the electron in 1897 was the first proof that the atom had any parts.

In the year 1900—an easy date to remember—came the greatest revolution that physics has ever known—the discovery of the quantum by Planck; and this marks the beginning of the third period in the relations of physics to chemistry. Up to that time all physics had been based on what we now call the classical mechanics of Galileo and Newton. This theory had arisen from the observation of the motion of visible bodies on the surface of the earth—weights and pendulums—and had then been extended to the planets, and shown to be equally true of their motions. It had sustained the whole triumphant march of physics through the ensuing two centuries. It was universally assumed, and as it seemed with complete justification, that these principles, which had been shown to apply alike to the motions of pendulums and of stars, were equally applicable to all kinds of matter, down to its smallest particles. But towards the end of the last century difficulties had arisen in applying these principles to certain classes of phenomena, especially to those dealing with the relations of radiation and matter. To give only one example: it could be shown on the classical mechanics that the energy of radiation must pass almost entirely into the shortest waves, so that the most intense radiations of a hot body should be in the far ultra-violet; while experiment showed that for ordinary hot bodies the maximum was in the far infra-red, and that even the light of the sun with a surface temperature of 6,000° has its greatest intensity in the yellow, as anyone can see by looking at it.

To meet these difficulties Planck put forward the quantum theory, of which the essence is that the interchange of energy does not take place continuously, but in separate steps or quanta, the size of which is not fixed like that of an atom, but is proportional—for radiation, at least—to the frequency of the oscillations or waves of which the energy consists. This theory, the truth of which has been completely established by the subsequent development of physics, leads to a remarkable conclusion. It applies of course to all bodies large or small, but in its practical results it leads to one conclusion for large bodies and another for small. The quantum itself is always, in comparison with quantities of energy that we observe in ordinary life, very minute. Thus of the quanta of yellow sodium light it would take 10^{16}—ten thousand million million—to heat a milligram of water one degree. It follows that when we are considering masses of matter and quantities of energy such as we can see or handle, the "steps" by which Planck replaced the continuous process of Newton are so small and so numerous as to make no practical difference. Hence for the mechanics of all such "macroscopic" quantities of matter the new theory leads to the same results as the old. This is indeed to be expected; the Newtonian theory has been verified for such bodies, and for them it is true; but for very small bodies, and especially for atoms, the steps become significant and the theory no longer holds. This is far from meaning that the new theory is of no practical importance. Our whole lives depend on processes which, although they occur with weighable quantities of matter, really depend on the simultaneous occurrence of an enormous number of atomic interchanges of energy, and these can only be interpreted by means of the quantum theory. It is precisely in chemistry that we have to deal with phenomena of this kind. The first direct evidence of the quantum theory, though of course it was not recognized as such at the time, is Dalton's law of multiple proportions. The "ratio of two small numbers," which we have to introduce in expressing this law, is the fundamental characteristic of the quantum theory. It was no accident, but a basic necessity, that made Ostwald's attempt to eliminate the atom break down when he came up against the laws of multiple and reciprocal proportions.

The recognition of the true mechanics of the atom was a necessary preliminary to any detailed knowledge of atomic structure. The main constituents of the structure had indeed been discovered without the help of the quantum theory, the electron in 1897 and the nucleus in 1911; but their interactions could not be worked out as long as the older mechanics of Newton and Maxwell was used. In fact, on these principles the nuclear model of Rutherford was impossible, and it was only after Bohr had shown how to apply the quantum theory to the atom that further progress could be made. How rapid this progress has been in the last 20 years we all know; it has finally broken down any distinction in subject-matter between physics and chemistry, and the elucidation of molecular structure has now become the task of both sciences.

This brief account of the services which physics has rendered to chemistry in the past may help us to realize the true relation of the sciences to one another. The opposition of extension and intension—the rule that the simpler the problem, the more completely we can solve it—still holds. If we call chemistry molecular physics, we may say that the physicist is applying his more deductive methods to its simpler aspects, while the chemist is simplifying its more complicated phenomena by observation and induction. The practical use of a discussion such as this, which is addressed primarily to chemists and not to physicists, is to get a truer conception of the way in which the chemist should pursue his subject, and of the extent to which he should be influenced by physical conclusions. On the latter point the position is clear; we are bound to make use of any physical weapon that is available for the solution of our problems. On our side we have a duty both to physics and to ourselves. In the first place we have to present to the physicist in a simplified form those questions arising out of our chemical experience which he is best able to solve. The multiplicity of chemical phenomena is so great that only those who have given their whole attention to the subject can really know the facts relevant to a particular chemical question. We have therefore to collect and coördinate the data bearing on the phenomena which are accessible to physical attack. We also have to remember that we chemists are, so to speak, responsible for all chemical compounds. The physicist selects a few compounds peculiarly suitable for his measurements, and acquires detailed knowledge about their structure and behavior. We have to review the whole field of chemistry, and to see how far these conclusions can be extended to chemical substances in general, and if they can not, to find if possible what chemical characteristics limit this application.

At the same time we have to go on with the work of educing general principles out of the great mass of chemical particulars. In the course of this process of simplification it is never possible to proceed very far without forming some idea of the actual mechanism which is at work, or in other words without forming some hypothesis and imagining some model of the molecule. The physicist proceeds in the same way; but his simpler problems, lying nearer to the ideal systems for which the complete dynamics can be worked out, make possible a more detailed theory and a more precise model. This does not mean that they are better than those of the chemist, if by better we mean more suited to the advancing of knowledge; there is a place in the growth of science for both. Every theory and every model is imperfect. As Bohr has pointed out, a model of an atom or molecule is a machine of macroscopic size which is supposed to behave in the same way as an atom or molecule. But such a model, owing to the magnitude of the energies and motions of its parts, will act according to the Newtonian laws of mechanics, while the atom is subject to the quantum restrictions. An exact agreement between the model and reality is therefore not to be expected; we can only try to make the differences as small as possible. This is the position of the Bohr model at the present moment. It is built on classical principles, and then a new condition is imposed, forbidding all forms of motion which do not comply with the quantum principles. This new condition is wholly arbitrary, in the sense that it does not follow from the construction of the model; but it is necessary in order to make the model work right.

This model has shown an amazing power of behaving like a real atom; the experimental results can be shown to agree with those predicted even in quite small details. But with the rapid development of atomic physics the model has not been found equal to every demand made upon it. This was partly due to the difficulty of calculating the behavior of such a model in any but its simplest forms; and so far we might hope that the difficulty would be removed by improvements in mathematical analysis. But there were more serious troubles; in certain respects the conclusions derived from the model were shown to be definitely wrong; for example, it represented the hydrogen atom as a disk, while it could be shown experimentally that it was a sphere. This does not necessarily mean that the model is entirely wrong, but only that it is imperfect. In the last few years a new method of attacking atomic structure has been developed, that of wave mechanics. This can hardly be said to involve a model at all; or if it does, it is an elusive form of the Rutherford nuclear atom, in which the stationary states of Bohr are maintained, without their physical meaning being clearly expressed, although it is mathematically defined. But whatever we may think of the new model, the efficacy of the mathematical calculus involved is indisputable; it makes it possible to predict a whole series of properties which were inaccessible by the older method, and which can be verified experimentally. It is obvious that the equations of the new wave mechanics express the truth very closely, and are of immense practical value; and we may hope that as our knowledge increases it will become possible to represent them by a definite model—perhaps some modification of the Bohr model—which will bring the structure more clearly before us.

I have discussed the atomic model at some length, partly because of its intrinsic interest, but largely because an understanding of the conditions and limitations of a physical theory will help us to grasp those of a chemical theory. A chemical theory, dealing with more complicated phenomena, is less accessible to mechanical treatment. It takes account in the first instance of properties which can not be measured quantitatively, but which are clearly shown to exist. It adopts some terminology to express these, without at first making any exact assumptions as to their physical meaning. This after all is what physics has done with the quantum; we do not know even now what the quantum limitation really means, although we know what effect it produces. As an example of a chemical theory consider the theory of structural chemistry. This in its original form assumed the existence of linkages between the atoms in a molecule, the nature of which it did not pretend to discuss, though it could make accurate statements as to their number, and as to the order in which the atoms were linked. It was capable of predicting the composition and many of the properties of the substances formed in innumerable organic reactions, and of consistent application to hundreds of thousands of organic compounds. "Chemists," as Helmholtz[4] said in 1891, "must be allowed to form hypotheses after their fashion, since the whole extraordinarily comprehensive system of organic chemistry has developed in the most irrational manner, always linked with sensory images which could not possibly be legitimate in the form in which they are represented." A direct result of these "sensory images," that is of the simple model of atoms joined by links of an unspecified physical nature, was the further development begun by van 't Hoff when he extended these ideas to three dimensions and opened up the new field of stereochemistry. As knowledge increased, new relations were discovered in the behavior of these links. Baeyer in his strain theory assumed that two links of one carbon atom had a "natural" inclination to one another, that given by the tetrahedral model, and that any departure from this involved a proportionate degree of instability in the molecule. This conclusion could not be deduced from the nature of the link, because that nature had not been physically defined; but it was justified by the fact that its consequences agreed with experiment.

During the further study of the reactions of organic compounds, it became possible to classify to some extent the effects which are exerted on the reactivity of certain atomic groups by other atoms or groups present in the same molecule. To express these conclusions new symbols were adopted—plus and minus signs, or thick and thin bonds. All these developments were perfectly legitimate if they made it easier to coördinate the results of experiment. No assumption had been made as to the physical meaning of the valence bond, and the new theories only implied

[4] Koenigsberger, *Life of Helmholtz* (English ed., Oxford, 1890), p. 340.

that this force of unknown character is found experimentally to be capable of certain modifications, which are expressed by the new symbols. This is typical of a chemical as opposed to a physical theory; it arrives by induction from experiment at a series of relations between the structures of molecules and their behavior, and shows that these can be simply explained by a small number of assumptions as to the forces between the atoms; but it makes no statement as to the physical meaning of these forces and their modifications.

At the time when these theories of reactivity in organic compounds were being developed, the physicists had arrived at a theory expressing the valence forces in terms of electrons; in particular G. N. Lewis had shown that the non-ionized links, with which the organic chemists were mainly concerned, could be ascribed to the sharing of the valence electrons, two to each link, between the atoms. This theory was itself in some degree symbolic; no one knew precisely what was meant by "sharing"—we are only now, 15 years later, beginning to learn what it means—but it was possible on the Bohr model to get some general idea of how it might happen, and as physicists were by this time able to count exactly the number of electrons in the atom and to determine what groups of electrons were stable, the Lewis theory could be extended very widely; and it was found to give satisfactory results, and to involve no assumptions as to the physical nature and behavior of electrons incompatible with physical experience.

It was quite evident that the explanation of the differences which the organic chemists had detected in the links must ultimately be found in the behavior of the valence electrons; and the organic chemists hastened to look for it there. But at this point we come upon a difficulty. As long as the chemist confines himself to his symbolic representations, he can do what he likes with them, so long as what he does helps him to classify and coördinate his ideas. But as soon as he claims to give them a physical meaning, he must recognize all the implications of a physical statement. Links or bonds may be strained, or thickened, or imperfectly saturated, or classified into primary and subsidiary, and the atoms they join may have a positive or a negative character, because these words correspond to real differences in behavior, and therefore to some change in the forces between the atoms, which we may hope to explain when we know what these forces are. But electrons must behave in certain ascertained ways, and the distribution of positive and negative electricity in a molecule is subject to physical laws and measurable by physical means. It cannot be denied that this requirement has sometimes been overlooked. It was said of one well-known theory of molecular structure, which did very good service in its day, that the author's electrons "have so few of the known properties of electrons that it is not immediately clear why they are called electrons at all"; and the same might be said with equal truth of some other theories.

Thus the transition from the chemical to the physical theory needs care. The ultimate object of the chemist is to express his conclusions in physical terms, but he must remember, if he tries to do this, that these terms have already a very elaborate and precise connotation; every concept which he uses involves a series of definitely established properties. That, in fact, is why it is so important to be able to use them. But it is essential to use them rightly. The chemist must not employ the language of physics unless he is willing to accept its laws. Within these laws a certain latitude of interpretation is left to him, and some tentative physical suggestions may be put forward unsupported by physical evidence, provided the physical evidence does not contradict them. On this last point no exceptions are allowed. The chemist must resist the temptation to make his own physics; if he does, it will be bad physics—just as the physicist has sometimes been tempted to make his own chemistry, and then it was bad chemistry.

If these points are clearly realized, the prospects of progress in chemistry are far more favorable now than they have ever been. The ultimate problem of the establishment of the relation between molecular structure and properties is open to attack from both sides, and these attacks are now converging. We have found that the mechanics of the atom is different in many ways from that of large bodies, and we—or they—have found what the mechanics of the atom is, or at any rate how its results can be calculated. Physics has already told us the "empirical formulae" of the atoms, the number of electrons which they contain and their dispositions. It has given us a mechanism of atomic linkage. It has provided us with methods of measuring many of the characteristic properties of the links between atoms, the distance between the atoms, the relative positions in space, the way in which the electrons are shared between the atoms, the work required for their separation. The problems before us are far too complicated to be solved by the physicist alone by deductive reasoning founded on experiments with a few selected compounds. But much of the information we need he has shown us how to obtain; if we coöperate heartily he will provide us with more; and in this way our theories can be tested and amended by physical measurements and physical reasoning at every step. All that is needed is a proper mutual understanding and good-will.

CHAPTER I

ATOMIC COHESION

THE main object of these lectures is to consider the nature of the covalent or non-ionized link between two atoms, and to discuss the various kinds of information which can be obtained about it, especially the distances between the linked atoms, the work required to separate them, the dipole moment of the link, and the angles which the several valences of a polyvalent atom form with one another. It may however be useful, before we go on to these points, to consider firstly the more general question of the forces which hold atoms together in matter,[1] and secondly (Chapter II) the conditions which determine whether two atoms form an electrovalent or a covalent link, and the much disputed question whether these two forms of linkage are essentially distinct or merely represent the extremes of a continuously varying series of states.

Modern physics has shown that the atom is made up of a nucleus and electrons, both charged electrically, and both in some degree massive. It is therefore subject to two kinds of forces, electromagnetic and gravitational, and, so far as we know, to no others. The physical analysis of nature has now gone so far that we have good reason for believing that the electromagnetic and the mass properties are the only ones that govern the attraction of matter for matter. All the various terms that were so familiar to the older chemists, cohesion, adhesion, affinity, valences primary and secondary, co-ordination, and so forth, must be regarded as expressing the results of electromagnetic or gravitational forces. And of these two, the only one which concerns us in chemical questions—in considering the interactions of masses of matter which are not too large to be handled in the laboratory—are the electromagnetic. The unit electrical charge, that of one electron per atom, is relatively enormous and gives rise to forces far greater than those due to the gravitational effects of the atoms on one another. Debye has pointed out that a gram-atom of sodium ions (23 grams) at the north pole of the earth would attract a gram-atom of chlorine ions (35.5 grams) at the south pole with a force equal to the weight of 52,000 kgm. At any given distance the electrical attraction between a sodium ion and a chlorine ion is 10^{33} times the gravitational. So we are left with the electromagnetic forces alone to account for all the properties of atoms and molecules.

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[1] An excellent summary of the position has been given by H. G. Grimm, *Z. Elektrochem.*, 34, 430 (1928), on which the following account is largely based.

It has been shown that these will account for the formation of definite valence bonds between atoms in two different ways: by the transference or by the sharing of electrons. Both of these involve specific changes of position or orbit of one or more of the relatively small number of mobile electrons that an atom possesses, the outer or valence electrons; and this is how the small integral values prescribed by the ordinary rules of valence arise.

But these are not the only ways in which atoms can attract one another. In addition to these two forms of attachment, electrovalence and covalence (with co-ordination as a sub-species of the latter), there is a third which, although it is of a less definite and so to speak individual character and cannot be included among the forms of valence, is yet of great importance.

Experiment shows that all molecules whatsoever, even the monatomic molecules of the rare gases, attract one another. It is this attraction which is expressed by the a of van der Waals' equation; and since no substance could exist in the liquid or solid form if a were zero, and every known substance can be solidified, it follows that this molecular attraction is a universal property of matter.

It is easy to see in general how this attraction arises. The positive and negative parts of which an atom or a molecule consists will be affected by those of any other atom in the neighborhood, like charges repelling and unlike attracting one another. This attraction does not amount to chemical combination; the electrons do not pass from one atom to the other, nor are they definitely shared between them; but still there is an attractive force between the atoms. This must be a property common to all atoms and all molecules, since they are all made up of nuclei and electrons. We therefore have to recognize a third form of force attaching atoms and molecules to one another. This is known as the van der Waals force.[3]

These three kinds of force, electrovalence, covalence and the van der Waals force, are all that it is necessary to assume as acting in gases, liquids, or solids.

The next point is to consider which of these are active in particular states of matter. There are of course many doubtful cases, where it is not possible to give a definite answer to this question, or not without a lengthy discussion of the properties of the material in dispute. But if we disregard these, and confine ourselves to well-marked groups, we can get a fairly clear idea of the various ways in which the chief classes of substances are held together.

We may begin with the salts, such as the alkaline halides. In the solid state these are crystalline substances, with high melting and boiling points. X-ray examination shows that they have a lattice in which the atoms are regularly disposed; in sodium chloride, for example, there are six sodium atoms round every chlorine, and vice versa. There is no sign that a sodium atom is more closely attached to one of its six neighboring chlorines than to any other, and we further have definite evidence that the atoms in the crystal are electrically charged, *i.e.* are ions.

It is clear that the crystal contains no sodium chloride molecules, but only a regular arrangement of ions, and that the force holding it together is of the first kind, electrovalent or electrostatic. This force is very powerful, and hence the work required to break up the crystal—the heat of evaporation—is very large, as the high boiling point shows. From Trouton's law—molecular heat of evaporation = absolute b.p. × 21.7, approximately—the heat of evaporation of sodium chloride (b.p. 1441°) must be about 36 kgm-cals per gram-molecule. In the vapor of the salt the ions are not all separated, but are present largely in pairs; to convert the solid into the wholly dissociated vapor would need 200 kgm-cals per gram-molecule. The molecules of NaCl which are still present in the vapor can be shown[4] to consist of ions, Na[Cl], held together as in the solid by their opposite charges (electrovalence). In the fused salt (we know much less about the liquid state than we do about the gaseous or the solid) it is to be presumed that we have a similar condition of complete ionization and partial dissociation.

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[3] The mechanism of the van der Waals force in gases was first discussed by Debye—*Physik. Z.*, 21, 178 (1920)—who calculated the mutual polarization of the atoms. Recently the subject has been further examined by the methods of wave mechanics, and it has been shown that the forces which Debye considered are responsible for only a part of the effect, and that the rest must be ascribed to a resonance of the orbits which can not be calculated by classical methods.

When the salt in question contains polyatomic ions, either what we generally call complex ions, as in a ferrocyanide or a platinichloride, or such ions as NH_4 or NO_3, we still have in the crystal an ionic lattice of the two kinds of ions, which are held to one another by electrostatic forces; but the atoms composing the polyatomic ion are themselves held together in the ion by forces of the second kind, those of covalence. This is confirmed by the results of X-ray examination, which show that in calcium carbonate, for example, each carbon atom is more closely related to its own three oxygen atoms than to the others.

The second main group of substances consists of the metals; but these offer great difficulties and are better considered after we have dealt with the third and last of the chief divisions, the substances which are neither salts nor metals, and which do not conduct electricity either in the solid or in the liquid state. This class includes most organic compounds and also the elements of the later periodic groups and their compounds with one another, such as nitrogen, chlorine, carbon dioxide, the paraffins, and so on. Here we have in the gaseous state definite molecules, the atoms of which are attached by covalent forces (Type II), while the molecules themselves show only a weak van der Waals attraction.

In the solid state there are two kinds of force at work: covalent forces holding together the atoms of each molecule, just as in the gas; while the molecules themselves are held together in the crystalline lattice by means of the van der Waal forces. This view is entirely confirmed by the X-ray examination of the crystals, which shows that the chemical molecule is essentially the unit out of which the crystal is built.

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[4] H. Sponer, *Z. Elektrochem*, 34, 483 (1928).

The weakness of the van der Waals forces between the molecules, as compared with the covalence forces within a single molecule, is proved by the work necessary to break up the structure. For example, with carbon tetrachloride (m.p. −23°, b.p. +77°) it has been found that to break down the crystal lattice and form the liquid needs about 7 kgm-cals; to convert the liquid into the vapor, that is, to separate the molecules completely from one another without separating the atoms in each molecule, needs about as much more; while to separate the atoms in the molecule from one another, thus overcoming the covalence forces, requires 270 kgm-cals (all these being calculated for one gram-molecule, or 154 grams). It is because of the weakness of attachment of the molecules to one another, and the small amount of work required to separate them, that these covalent non-ionized substances usually have such low boiling points.[5] For the same reason the crystals of such compounds as a rule are softer than those of salts.

For completeness we may add the rare gases, in which the forces are entirely of the third (van der Waals) kind, in the gaseous, liquid and solid states.

The structure of metals presents a problem that has not yet been completely solved. They form a group apart. They occur with elements which can give monatomic cations, and with solid solutions or compounds of such elements among themselves. Their physical properties are quite peculiar, especially their invariable opacity to light (except in the thinnest films), and their power of "metallic" conduction, *i.e.* of conducting electricity without the simultaneous transport of matter which accompanies the conductivity of electrolytes. Soon after the discovery of the electron Drude propounded a theory in which it was assumed that a metal contained free electrons in a state like that of a gas, which were capable of diffusion, so that under the influence of a potential gradient they would drift in the direction of the positive pole. This was open to the objection that such electrons should have a specific heat equal (particle for particle) to that of the cations which were formed by their liberation, whereas, as we know, the atomic heat of an element is much the same in the metallic state as in its compounds. To avoid this difficulty Lindemann suggested that the metal, which in the solid state is undoubtedly crystalline, formed two interpenetrating space lattices just as sodium chloride forms two interpenetrating lattices of Na^+ and Cl^- ions; and that in the metal, while the positive lattice consisted of positively-charged atoms (cations) as in the salt, the negative lattice was formed of electrons which could move as a whole, with a certain amount of distortion indicated by the electrical resistance, through the positive lattice under the influence of a potential gradient. This theory, which is in many ways very attractive, is not wholly supported by the results of a wave-mechanical discussion of the problem by Sommerfeld,[6] Heisenberg, and others. Their conclusions, which have not yet been developed in detail, are difficult to express in simple language; but they indicate that the electrons which carry the current in a metal, the number of which is still undetermined, behave as a "degenerate gas" (rather like helium at very low temperatures, whose properties depart in many ways from those of an ordinary gas), but must be supposed to have a free path of the order of 100 times the atomic diameter. A remarkable confirmation of this is afforded by the observation that the least amount of an impurity which, under favorable conditions, can measurably reduce the conductivity of a metal is one atom in a million. In such a mixture every hundredth atom in a row is an atom of the impurity; and it is obvious that this amount is just enough to interfere with the motion of the electrons, and therefore with the conductivity, if the mean free path is 100 atomic diameters. So far as the electrons in a metal can be regarded as really free, they must of course produce a corresponding number of positively charged atoms or cations, and these oppositely charged particles will be held together by electrostatic attraction (Type I); but there is some reason to think that some of the valence electrons in a metal, or all of them for some of the time, may form covalent links (Type II). An argument in favor of this is afforded by the observed distances between the atoms in a metal. Further details are given later,[7] but the argument may be outlined here. The distance between two atoms in a molecule, which is highly characteristic of the atoms but which also depends on the mode of linkage, is usually expressed as the sum of two "effective radii". There is good evidence that the effective radius of an atom is greatly affected by its charge, being increased by a negative and diminished by a positive charge, as we should expect on general principles. For example, the effective radius of the neutral or covalent fluorine atom is 0.68Å and that of the F^- ion 1.33Å; that of neutral silver is about 1.5 and that of the silver ion Ag^+ is 1.13. Now it is always found that the radius in the metal (half the distance of nearest approach) is very close to that of the covalent atom, and much greater than we should expect if the atoms were in the ionized (cationic) state; for example, the radius in metallic silver is 1.44, in metallic sodium it is 1.86, the radius of the sodium ion being 1.0 Å. This suggests that the linkages between the atoms in a metal, or most of them, are covalent; but that under the conditions prevailing in a metal the linking electrons can to some extent break free from their positions and serve as carriers of the current. The question is still obscure, and at present most wave mechanicians prefer to assign the metallic link to a separate class alongside of the electrovalent and covalent classes.

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[5] Compare lithium fluoride (mol.wt. 26, b.p. 1676°) and tellurium hexafluoride (mol.wt. 241, b.p. −35°).

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[6] For a more or less popular account, see A. Sommerfeld, *Ber.*, 61, 1171 (1928).

There can be no doubt that definite intermetallic compounds exist; some can even be shown to be present in the vapor phase; and in these we cannot doubt that the atoms of the compound are united by covalent forces into molecules, the attachment of these molecules to one another in the solid alloy being of the metallic kind, whatever that may be.

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[7] Chapter III, pp. 86, 88.

We have now dealt with the three great classes of substances: salts, metals, and covalent compounds. We have seen how the first owes its existence in the solid state to electrostatic forces, while with the third the atoms in a molecule are attached covalently and the molecules themselves are held together in the solid state by the van der Waals forces of their external fields. The state of the metals is less certain, but there is some reason to think that in them also the covalent forces play a large part.

There still remain, however, certain classes of compounds which do not exactly fit into any of these categories. One of the most interesting is that typified by the diamond. The physical properties of the diamond, such as its great hardness, its transparency, its non-conduction, and its enormously high melting and boiling points, are familiar. X-ray investigation shows that it consists of a series of atoms all occupying exactly similar positions, each being placed between four neighbors which are at the points of a regular tetrahedron of which the particular atom under consideration forms the center. This structure runs through the whole crystal. It is clear that the attachment between the atoms is of the second or covalent kind, since carbon practically always forms covalent links, and we know already from organic chemistry that the most probable position of four groups covalently attached to a carbon atom is at the points of a regular tetrahedron. Moreover it has been shown that the distances between the atomic centers, and the work required to separate two atoms, are practically the same in the diamond as in the carbon chains of organic compounds.[8] But the crystal structure does not indicate any division into molecules at all; the whole lattice is continuous, and every atom is the same distance from its four neighbors as every other. The only conclusion we can arrive at is that the whole crystal is one molecule; that the covalent links run without a break through the whole mass, and that the only forces acting are those of covalence. This explains the extreme hardness of the diamond, since it can be cut only by the actual breaking of the covalent links, and moreover the structure is very strongly strutted, as is obvious from the model. It also explains the non-volatility, since the substance can volatilize only by chemical decomposition. Substances of this kind are known as "giant molecules". Recent work[9] has shown that they are more numerous than was supposed, especially among compounds of the general composition AB where the sum of the valences of A and B is 8, as in carborundum (CSi), silicon, aluminum nitride, and beryllium oxide.

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[8] See Chapter III and Chapter IV.

A very interesting substance from this point of view is the allotropic form of carbon, graphite. It has always seemed extraordinary that while diamond is the hardest of known substances, graphite is in a sense the softest; it is the only solid that can be used as a lubricant. The examination of the crystal structures makes the reason clear. The two structures are in many ways very similar; but whereas in diamond every atom is the same distance from all its four neighbors, in graphite it has the same relation (much the same as in diamond) to three of them but is more than twice as far from the fourth.[10] The result is that in graphite we have a series of layers one atom thick, in each of which the carbon atoms are as firmly linked as in diamond (and by the same covalent forces, at nearly the same distances), but each layer is some distance from the next. This accounts for the mechanical peculiarities of graphite: the atoms in each layer are firmly enough bound, but the layers are easily detached from one another, giving a series of little plates only one atom thick, which make an admirable lubricant.

We thus have in graphite a series of plates, each of which may be called a giant molecule in two dimensions, its atoms held together by covalence forces. The force which holds the plates together is less certain. Graphite, unlike diamond, is a conductor of electricity and hence it is commonly assumed that the electrons (one to each carbon atom) which link the layers together are in the same state as in metals. This may probably be so; but it is remarkable that while we find the interatomic distances in metals to be those required for covalent linkage, these links in graphite are more than twice as long as those between covalently linked carbon atoms.

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[9] H. G. Grimm and A. Sommerfeld, *Z. Physik*, 36, 36 (1926).

[10] The distances are: in diamond, 1.54; in graphite 1.42, and 3.3 Å.

Other instances of such "layer lattices" (*Schichtengitter*) are known among compounds, as with zinc iodide. Here it can be shown[11] that the crystal (like graphite) consists of a series of layers somewhat remote from one another and easily separated. Throughout each layer the linkage is purely covalent (including co-ordinate links), and here the forces between the layers are no doubt of the van der Waals type.

We can even carry the process a stage further and get a one-dimensional giant molecule, if the recent views of the structure of cellulose put forward by Meyer and Mark[12] are correct. It is probable that in cellulose we have a long series of sugar molecules joined together by loss of water, that is by the formation of an ether grouping C—O—C, thus forming a thread one molecule (about 8 Å.) thick. This gives a molecule of indefinite length, whose atoms are held together entirely by covalent links. The actual fiber of the cellulose is made up of a number of these side by side, the attachment in the two last dimensions being effected by means of van der Waals forces, or perhaps by association (co-ordination) of the hydroxyl groups.

This discussion raises a further question of some importance. A theory of valency should be able to account for the structures of all known molecules; but as we have seen there is a force by which atoms and molecules attract one another, the van der Waals force, which is of a more diffuse nature than the true valence forces, and is not to be expected to conform to their laws. It is evident that these laws will apply only to groups of atoms held together by the valence forces of electrovalence and covalence, and the question arises how such true molecules can be distinguished in practice from aggregates whose parts are held together only by the van der Waals forces.

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[11] F. Hund, *Z. Physik*, 34, 833 (1925); V. M. Goldschmidt and co-workers, *Geochemische Verteilungsgesetze* (Oslo, 1926), VI.

[12] K. H. Meyer and H. Mark, *Ber.*, 61, 593, 1928; *Aufbau der hochpolymeren Naturstoffe* (Berlin, 1930). [*See also* Pringsheim, this SERIES, Vol. 6 (1932), pp. 366ff.—Ed.]

We commonly distinguish a compound by its having a definite stoichiometric formula—one with a limited number of atoms—and especially by the fact that this remains constant independently of changes of the pressure, temperature, and concentration under which it separates in its formation.[13] The argument is that the simple numerical ratio of the various atoms in the phase, which is what we mean by a stoichiometric formula, can be secured only by the action of forces which attach atoms in small numbers to one another in molecules, *i.e.* by valence forces.

To this argument there is however one serious exception. It is perfectly sound when applied to liquids and gases; but in the important case of crystalline solids there is another way in which these simple relations can arise, and that is by the geometrical requirements of the crystal lattice. X-ray analysis shows that a crystal is formed by the repetition of a series of precisely similar units, the crystal units or crystal cells. Where the size of the molecule is known from other evidence, for example with benzene, we usually find that the unit cell contains not one molecule but several, two or four or even more. With many substances, as with benzene itself, it is clear that the molecules in the cell are attached by van der Waals forces and by these alone, just as the cells are themselves. Now there is no reason why there should not be crystals whose cells contain molecules of different kinds, held together in the same way as the molecules in solid benzene, that is by van der Waals forces and not by true valences. If these different kinds of molecules are similar in size and in the distribution of their external fields, it may make very little difference whether the crystal unit of, say, four molecules is all A, or three molecules of A and one of B, or two of each; and in that case we get the phenomenon of solid solution, where the proportion of A to B in the solid varies continuously with that in the liquid in equilibrium with it. In other cases the two sorts of molecules may be quite different and yet there may be a particular proportion, say $3A + B$, which packs into the crystal and satisfies the van der Waals forces peculiarly well. The composition of such a crystal would be given by the sum of the formulas of the molecules in the cell and would still be comparatively simple, because the number of such molecules is small. But not all the atoms in this formula would be held together by valences; they would form a series of separate molecules. We are, therefore, not justified in concluding that the empirical composition of a solid phase, even when it gives a stoichiometric formula independent of changes in the temperature and composition of the liquid from which it separates, is that of a single molecule.

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[13] The classical negative example is the constant boiling mixture of hydrochloric acid and water.

The question can only be answered satisfactorily by getting evidence of the existence of the compound in the gas or the liquid, where these crystalline forces do not interfere. The difficulty is peculiarly great when the solid contains molecules of the solvent from which it separates,[14] because determinations of molecular weight in solution do not tell us whether the solute is combined with the solvent or not. Among the great class of hydrates we know that there are many in which the water has entered into real chemical combination; but in others there is good evidence that no true combination occurs; that the water (or ice) molecules are held by the van der Waals forces in the crystal along with those of the salt or other solute; and that the simple numerical ratio of the different kinds of molecules merely reflects the geometrical regularity of the crystal.

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[14] The most striking examples are the solid hydrates of the paraffins and, still more, those of the inert gases. Compare de Forcrand, *Compt. rend.*, 135, 959 (1902); *ibidem*, 181, 15 (1925).

CHAPTER II

ELECTROVALENCE AND COVALENCE

BEFORE we can discuss the detailed nature of the covalent link we have to consider its general relation to the electrovalent or ionized link, and the conditions that determine which of the two is formed by a given pair of atoms. A further question is whether these two forms of linkage are essentially distinct, or are only the extremes of a continuous series of states. This will be discussed in detail later in this chapter, but for the present it will be assumed that they are distinct.

We have first to deal with the electrovalent link. In the earliest systematic treatment of this question Kossel regarded the ions practically as rigid structures.[1] This view, which was natural and reasonable in a first survey of the subject, was soon shown to need considerable modification. The simplest proof of the inexactness of this "billiard ball" theory was afforded by the measurement by X-rays of the distances between the atomic centers in the alkaline halides, which were made by W. H. and W. L. Bragg. Most of these salts have the same (NaCl) lattice and so, if the ions are rigid structures, the difference of the interatomic distances in, say, the lithium and potassium salts of any halogen ought to be the same whatever the halogen, being the difference between the radii of the lithium and potassium ions. Experiment showed that this was roughly but not accurately true, as can be seen from the following table in which all the salts mentioned have the same sodium-chloride lattice:

	F	Cl ✓	Br	I
Potassium	2.664 ✓	3.138	3.285	3.525×10^{-8} cm.
Lithium	2.040	2.566	2.745	3.037
Diff.	0.624	0.572	0.540	0.488

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[1] Kossel pointed out, however—*Ann. Physik*, 49, 229 (1916)—that in the salt they must to some extent deform one another.

It will be seen that while the differences remain approximately the same, they show a very definite diminution with increase of the atomic weight of the halogen. Many other facts might be quoted which support this conclusion, that the ions cannot be regarded as rigid structures, but have some power of deforming one another.

The further investigation of the problem was made possible by the work of Debye[2] on the mutual polarization of the molecules of a gas. That such polarization should occur is to be expected. The atom, to take the simplest case, consists of a positive nucleus surrounded by negative electrons. In the isolated atom the center of action of the positive and negative electricities is the same. But if the atom is placed in an electric field, for example between two oppositely charged plates, the positive part, the nucleus, will be attracted towards the negative plate and the negative part, the electrons, towards the positive, and the atom will be polarized or deformed. That such deformation actually does occur is proved by the Stark effect, the shifting of the lines of a spectrum when the emitting atoms are in an electric field, owing to the distortion of the electronic orbits.

When the atoms are electrically charged—when they are ions—the field in their neighborhood is very powerful and we should expect the distortion also to be large. The actual amount of distortion which is produced in a given salt molecule will depend on two separate factors: the deforming power or strength of field of one ion, and the sensitiveness of the other ion to deformation—the extent to which it is deformed by an electric field of given strength. These two factors can be investigated separately, and we may consider the latter first.

If an atom or molecule can be polarized by an electric field, it must be polarized by light waves, since these are electromagnetic waves; and if this occurs the polarization will delay the progress of the waves, or in other words increase the refractive index of the medium. It was by considerations of this kind that H. A. Lorenz deduced, from the electromagnetic theory of light, the relation between the polarizability of the particles of a medium and its refractive index for infinitely long waves. The polarization p is proportional to the strength I of the electric field, and their ratio p/I is the polarizability, α. The polarization itself consists, as we have seen, in a separation of the centers of the positive and negative electricity of the molecule, which means that under the influence of the field the molecule or atom becomes an electrical dipole; it is equivalent to a rod with a positive charge at one end and a negative charge at the other. The effect is measured by the moment of the dipole produced, which is the product of the magnitude of one of the charges, which we may call e, into the distance l separating them. Thus $\alpha = el/I$, where I is the intensity of the field. Lorenz showed that if n is the refractive index of the medium for infinite wave-length, and N the number of molecules in a gram-molecule (6.06×10^{23}), the polarization is given by:

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[2] Debye, *Physik. Z.*, 21, 178 (1920).

$$\alpha = \frac{p}{I} = \frac{e \times l}{I} = \frac{3}{4\pi N} \times \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} = \frac{3}{4\pi N} \times R,$$

where M is the molecular weight, d the density and R the ordinary constant for the molecular refractivity on the Lorenz-Lorentz formula.

In this way we can calculate from the refractive index and the dispersion, the value of n, the refractive index for infinite wave-length, and so that of R, and so ultimately that of α, the polarizability.[3]

As far as the inert gases are concerned the measurements are simple, as they can be made directly on the gas. When we come to ions, the problem is less easy. We cannot obtain the ions as a gas. We can measure the refractive index of a solution with great accuracy, and by extrapolating the values of the molecular refractive power of the salt to infinite dilution we can eliminate the influence of the ions on one another. When we do so we find, as with the molecular conductivity, that the value of R_∞ is strictly additive (with an experimental error not exceeding 0.02 per cent) for the ions present. Two difficulties however still remain:

(1) We cannot determine the value of R_∞ for one ion, but only the sum of the values for the positive and the negative ions.

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[3] The correction of the refractive index from optical to infinite wave-length need not concern us here. It is further discussed under dipole moments in Chapter V, p. 132. For practical purposes it is usually sufficient to take the refractive index for visible light.

(2) The value obtained is not that of the "naked" isolated ions; it includes the effect of the ions on the polarizability of the neighboring water molecules—the effect of their hydration in any sense of that term.

These difficulties cannot be completely overcome, but we can approximately eliminate them in various ways.[4] The first difficulty was got rid of by assuming that the deformability of the hydrogen ion, since it consists of a single proton, is zero. As all other simple ions can be referred to hydrogen ion, and as we are mainly concerned with differences, this assumption enables us to determine without serious error the values for the ions in general. The effect of the hydration is less easy to allow for; but by various theoretical arguments an approximate value was obtained. This effect is not large, and even in the extreme case of the hydration of the hydrogen ion (*i.e.* the difference between H_2O and H_3O^+, or $2H_2O$ and $H_5O_2^+$) amounts to only -0.67, the actual values for ions in general being of the order of 10 units. The conclusions can be checked, for certain ions, by the theoretical calculation of their refraction from the spectral terms; and on the whole the agreement is good.

TABLE I

Refractivity of Gaseous Ions.

E.A.N.[a]	✓ 10	O^{--}	F^-	Ne	Na^+	Mg^{++}	
		7·0	2.4	1.0	0.5	0.3	
E.A.N.	18		Cl^-	A	K^+	Ca^{++}	Sc^{+++}
			9·0	4.2	2.2	1·3	0.9
E.A.N.	36		Br^-	Kr	Rb^+	Sr^{++}	
			12.6	6.3	3.6	2.2	
E.A.N.	54		I^-	X	Cs^+	Ba^{++}	La^{+++}
			19.0	10.3	6.1	4·2	3·3

[a] The effective atomic number, *i.e.* the actual number of electrons in the ion.

These being the methods used, it remains to consider the results. The values corrected in this way for a series of ions in the gaseous state are contained in Table I; they are given to one place of decimals, which perhaps is as far as their absolute magnitudes are to be trusted, in view of the various approximations involved. The results are plotted in Figure 1.

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[4] See J. A. Wasastjerna, *Z. physik. Chem.*, 101, 193 (1922); *Soc. Sci. Fennica, Commentationes Phys-Math.*, 1, 37 (1923); K. Fajans and G. Joos, *Z. Physik*, 23, 1 (1924); M. Born and W. Heisenberg, *Z. Physik*, 23, 388 (1924); Fajans, *Radioelements and Isotopes* (This SERIES, vol. 9, New York, 1931), Chapters IV, V, VI.

These values give the extent to which the various ions are deformed by a constant electric field. The first point to observe is the enormous effect of the ionic charge on atoms of the same effective atomic number (E.A.N.), or in other words, of the nuclear charge where the number of electrons is the same. A fall of 1 in the positive charge of the nucleus nearly doubles the polarizability. This is to be expected, since the increase of the nuclear charge, that is of the field in which the electrons are moving, fixes their orbits more firmly. The practical result is that when we come to consider the deformation of the ions of a salt by one another, the deformation of the cation may be taken to be usually negligible in comparison with that of the anion.

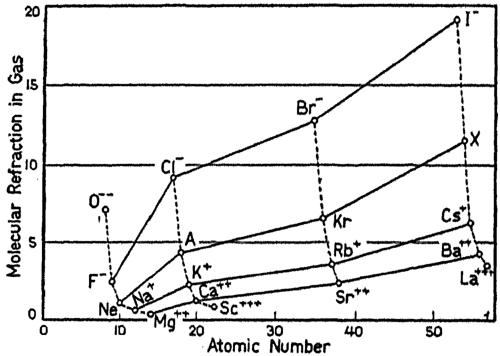

FIG. 1

The second point is that in any series with constant ionic charge the deformability increases with the atomic number, or in other words with the size of the atom, since in any periodic group these properties go together.

These are the main conclusions as to the deformability of the monatomic ions: that it is much less for cations than for anions, and that for ions of any given type it increases rapidly with the atomic size or atomic number.

Our ultimate object is to find the extent of deformation of one ion by another, in a single molecule or ion-pair of a salt. This is a more difficult matter. The polarization of single molecules can be examined directly only in the gaseous state; and as true salts volatilize only at temperatures so high as to cause a considerable amount of dissociation, practically the only vapors we can examine are those of covalent compounds, where the conditions are different owing to the covalence formation. We therefore have to rely on indirect considerations.

Some idea, however, of the way in which the deforming power of a cation varies may be got by calculating the field of the cation as measured by the ionic charge divided by the square of the ionic radius.[5] This enables us to compare ions of the same type, *e.g.* of inert gas structure. Some examples are given in Table II.

TABLE II

Field Strengths of Cations.

Li^+	1.7	Be^{++}	16		
Na^+	1.0	Mg^{++}	3.3	Al^{+++}	9.2
K^+	0.6	Ca^{++}	1.8	Sc^{+++}	4.4
Rb^+	0.5	Sr^{++}	1.2	Y^{+++}	2.7
Cs^+	0.4	Ba^{++}	1.0	La^{+++}	1.0

The basis on which the ionic radii are calculated is discussed in Chapter III, page 75.

It is evident from the figures given in Table I that the deformation which occurs is essentially that of the negative ion. It is also clear how the amount of deformation under a constant deforming force will vary with the nature of this anion. It will be more deformed the larger its ionic charge, and also the greater its size or atomic number. The ionic charge of the anion will indeed have a double effect, increasing the deformability in a given electric field, and in the salt increasing also the strength of the field. Thus the amount of deformation suffered by the anion in the salt will be greater the greater its ionic charge, and the greater its size.

The cations, as we have seen, will act essentially as deforming agents, the deformation they themselves suffer is usually negligible. Their deforming power will obviously increase with their ionic charge; it will also be affected by their size, but in the opposite sense to the deformability of the anions. The smaller the cation is, the nearer its charge comes to the anion, and the more effect it produces. Hence the cations are more effective the greater their charge and the smaller their size or atomic number. Another difference has to be considered here. Monatomic cations can be divided into classes according to the size of their outer electronic groups. Those which are given on Table I are all of what is called the inert gas type: they have the same number and arrangement of electrons as the inert gases, with an outer group of 2 or 8; all monatomic anions belong to this type. But we also have other types of cations, such as those of the B subgroups of the Periodic Table (Ag^+, Zn^{++}, In^{+++}, etc.), with an outer group of 18; those with two electrons more than this, such as Tl^+ and Pb^{++}; and the cations of the transitional elements (Cr^{++}, Cr^{+++}, Fe^{+++}, Ni^{++}, etc.) in which the outer group is more than 8 and less than 18. Experience shows that of all these types the inert gas type has the least and the B type (18) probably the most deforming power.

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[5] V. M. Goldschmidt, *Geochemische Verteilungsgesetze* (Oslo, 1926), VII, p. 60.

The evidence for these conclusions is of various kinds. We can discover the degree of deformation from the refractive power itself in the salt. It can be shown that if the anion is deformed by the action of the cation, its further deformability is diminished—its polarizability grows less—as we should expect, since the electrons are already to some extent controlled and restrained by the positive cation. The polarizability of the cation, conversely, is increased by the influence of the anion, whose negative charge to some extent frees the electrons of the cation from the control of their own nucleus; but the polarizability of the cation is so small in any case that this effect usually can be neglected.

We can thus discover the amount of deformation which one ion produces in the other by comparing the sum of the refractive powers for the isolated ions with the observed value from the refraction of the solid salt. In Table III R_{gas} is the value for the sum of the free ions (obtained from the solution values by eliminating the effect of hydration), and $R_{cryst.}$ the value obtained from the observed refractive index of the crystal. The differences ($R_{gas} - R_{cryst.}$) are plotted in Figure 2.

It will be seen that the change in going from the gas to the crystal is nearly always a fall, which is greater the

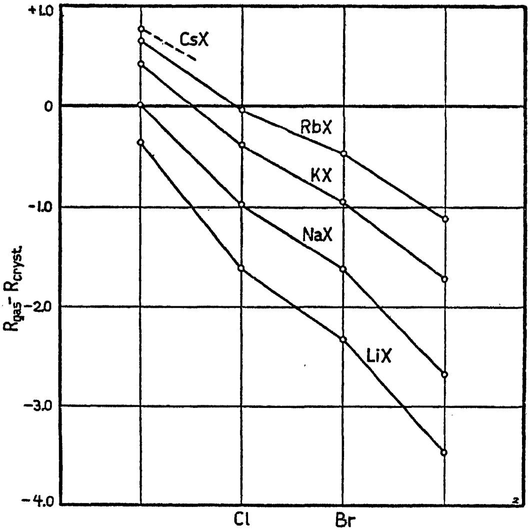

FIG. 2

TABLE III[a]

Refractive Power in Gas and Crystal.

		F ✓	Cl	Br	I
Li	R_{gas}	2.70	9.20	12.87	19.44
	$R_{cryst.}$	2.34	7.59	10.56	15 .
	Diff.	−0.36	−1.61	−2.31	−3.46
Na	R_{gas}	3.00	9.50	13.17	19.74
	$R_{cryst.}$	3.02	8.52	11.56	17.07
	Diff.	+0.02	−0.98	−1.61	−2.67
	R_{gas}	4.73	11.23	14.90	21.47
	$R_{cryst.}$	5.16	10.85	13.98	19.75
	Diff.	+0.43	−0.38	−0.92	−1.72
Rb	R_{gas}	6.08	12.58	16.25	22.82
	$R_{cryst.}$	6.74	12.55	15.78	21.71
	Diff.	+0.66	−0.03	−0.47	−1.11
Cs	R_{gas}	8.74			
	$R_{cryst.}$	9.51			
	Diff.	+0.77			

[a] Fajans, *Z. physik. Chem.*, 130, 729 (1927).

smaller (more deforming) the cation and the larger (more deformable) the anion. In a few salts with large cations and small anions (KF, CsF, RbF) the change is in the opposite direction, since the effect of the anion in deforming the cation and making it more polarizable, predominates. This effect is more marked in the oxides of the alkaline earths, as is shown in Table IV.

TABLE IV

Refractive Power in Gas and Crystal of Oxides of Alkaline Earths.

	BeO	MgO	CaO	SrO	BaO
R_{gas}	7.1	7.3	8.3	9.2	11.3
$R_{cryst.}$	3.3	4.5	7.4	9.4	12.6
Difference	+3.8	+2.8	+0.9	−0.2	− 1.3

The greater deforming effect of the cations of the B metals is shown by a comparison of the distances between the atomic centers in the crystals for the corresponding halides of sodium and silver. The salts given in Table V all crystallize in the sodium-chloride lattice, the values for silver iodide being obtained from a solid solution of this structure.

TABLE V

Atomic Distances of the Halides of Silver and Sodium, in Ångström Units

	F	Cl	Br	I
Silver	2.46	2.77	2.88	3.05
Sodium	2.31	2.81	2.98	3.23
Difference	+0.15	−0.04	−0.10	−0.18

While there can be no doubt that the cations which, like those of the B metals, are not of the inert gas type have a greater deforming power, the attempt to work this out in detail by the methods which are successful with the inert gas ions leads to anomalies, owing no doubt to the compounds in question having gone over from the ionized to the covalent state, with effects on the refractive power which we do not yet fully understand.

Thus the investigation of the deformation of the ions in a salt leads to these simple rules: The amount of the deformation is greater (I) the larger the ionic charge; (II) the smaller the cation; (III) the larger the anion; (IV) for cations of other types than for those of the inert gas type.

The importance of these rules lies in the fact that experience shows that the greater the deformation which an atom in a compound would be expected to undergo if it were ionized, the more likely it is to pass over into the covalent state. If we consider that the electronic orbits of the atoms in a salt are separate from one another, while in a covalent compound they interpenetrate, a view for which there is much support, we can see that the greater the distortion which the ions undergo, the more readily they will change their condition.

The experimental evidence for the conclusion that these four "Fajans rules" will always tell us which of two similar compounds is likely to be ionized, and which to be covalent, is very wide. Many examples have been given by the writer,[6] and some of the more striking may be briefly repeated here.

Rule I: *Influence of the ionic charge.* Restriction of ionization to elements of low valence, the earliest and latest groups of the Periodic Table, and the transitional elements which can exist in a low state of valency; the increase of hydration of ions with increase of valence, *e.g.* CsCl, anhydrous; $BaCl_2$, 1 and 2 H_2O; $LaCl_3$, 6 and 7 H_2O.

Rule II: *Effect of size of cation.* Ionization extends to elements of higher valence in the later than in the earlier periods of the Table, as is shown by the list in Table VI

TABLE VI

Li	Be	B	C
Na	Mg	Al	Si
K	Ca	Sc	Ti
Rb	Sr	Y	Zr

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[6] N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford, 1927); see especially pp. 104–8, 117, 153, 191–2, 258.

where the dotted line marks off the area of ionization, and passes through those elements whose tendency to ionize is weak.

Further evidence is given by the crystal structure; for example, BeO and AlN have covalent lattices, while MgO and ScN have ionic. In the same way $AlCl_3$ is not ionized in the fused state, while $ScCl_3$ and YCl_3 are.

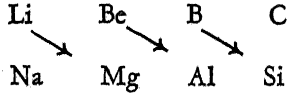
Rule III: *Influence of size of anion.* Among the halogens the formation of covalent compounds should be easiest with iodine and most difficult with fluorine. This is exemplified by the boiling points of the fluorides of aluminum and tin as compared with those of the other halides of these metals (see page 52). Again the formation of trihalogen ions, $[hal_3]^-$, is easiest when the linking atom is iodine; scarcely any trichlorides $M[Cl_3]$ exist and no trifluorides $M[F_3]$. Silver fluoride, chloride, and bromide form only ionic lattices, but the iodide also forms a covalent lattice.

Rule IV: *Smaller deformation by ions of inert gas structure.* The alkaline halides are all ionized even in the gaseous state: cuprous chloride, bromide, and iodide all have covalent lattices; silver chloride and bromide have ionic lattices (Rule III), but silver chloride has been shown to be covalent in the vapor (see page 58). Again, among the elements of Group II calcium, strontium and barium chlorides are all strong electrolytes in water, while cadmium chloride is a poor electrolyte and mercuric chloride almost a non-conductor.

The so-called "diagonal relationships" in the Periodic Table—the resemblances which an element shows to the element in the next higher group in the next period—such

TABLE VII

The "diagonal relationships".



as are indicated by the arrows in Table VII, are largely, though not wholly, due to the fact that as cations these elements increase in deforming power with increase of valence as we go to the right (Rule I) and diminish as we go to the lower period (Rule II); and these changes more or less neutralize one another.

Just as the ions were originally treated as rigid structures, so it was at first assumed that in the covalent link the two electrons were equally shared between the linked atoms. From this it would follow that the covalent link has no dipole moment.[7] It has, however, become evident that in general this is not the case. Except where the two atoms are the same, the sharing of the electrons is unequal; one atom has more, and the other less, than half of the charge. The degree of inequality can be determined by the measurement of the dipole moment[8] by one or other of the methods which have been so greatly developed in recent years. It is interesting to see what this inequality amounts to in some simple molecules. For example, hydrogen chloride is undoubtedly covalent in the gaseous state. The distance between its atomic centers has been determined from the absorption spectrum of the gas,[9] and is 1.273 Å. Hence the ionized molecule, if we can assume the charges to be localized on the two nuclei, will have a moment of $1.273 \times 4.774 \times 10^{-18} = 6.08 \times 10^{-18}$ E.S.U. The observed moment is 1.03, which is 17 per cent of this. The other halogen hydrides have a still smaller inequality, as

TABLE VIII

Link	d	$4.774d$	$\mu_{obs.}$	$\mu/4.774d$
H–Cl	1.273	6.08	1.03	16.9
H–Br	1.410	6.73	0.78	11.6
H–I	1.605	7.66	0.38	5.0
C–Cl	1.83	8.74	1.5	17.2

is shown in Table VIII, to which the C—Cl link has been added, the value assumed for its moment being that calculated on page 88; d is the distance in Ångströms between the nuclei, and μ the observed moment in E.S.U. $\times 10^{-18}$. These facts show that the original hypothesis of equal sharing is not accurately true, but it would seem that the inequality is usually not more than 20 per cent.

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[7] The co-ordinate link would have a moment of $e \times d$, where d is the distance between the two atoms.

[8] See Chapter V. [9] See Chapter III.

In order to see how far the ionic and covalent links are essentially distinct in their effect on the dipole moment, we ought to know how much the moment of a salt molecule (an ion-pair) is reduced by the deformation of its ions. Unfortunately we cannot measure this, because salts do not dissolve in non-polar solvents like benzene, and their vapors are too largely ionized for their dielectric constants to be determined.[9a] But we can get a rough idea in the following way. If we compare the distances between the atomic centers in two salts $A'B'$ and $A''B''$ (where the strokes indicate the valence and A' and A'' belong to the same period, and also B' and B''), *e.g.* NaF and MgO, or KCl and CaS, or RbI and SrTe, we find that the increase of the charge on the ions causes a contraction of about 9 per cent. We may not assume that the change of the dipole moment is proportional to this, but it is probably not very much larger; so we may suppose that in a uni-univalent salt the moment diminishes by about 10 per cent, and in a di-divalent salt pair by about twice as much.[10]

We can thus conclude that in ionic linkage the deformation may cause the dipole moment to shrink by some 20 per cent; while in the covalent link the unequal sharing of the electrons may lead to a residual moment amounting to as much as 20 per cent of the original moment of the undeformed pair of ions.

There thus appears to be a marked difference in the effect of the two kinds of linkage on the dipole moments; but of course it is not impossible that we might find extreme cases that would bridge over the gap.

It often has been assumed that the two names "electrovalent" and "covalent" only describe extreme examples of a continuous series of states, and that the covalent link is nothing more than a highly deformed electrovalent link. This view has been put forward, for example, by Fajans and by G. N. Lewis.[11] Evidence has accumulated, however, in recent years which strongly supports the opposite view, that there is an essential difference between the two kinds of linkage. Before we come to consider this it should be made clear that the link between two atoms can undoubtedly pass, with a change of conditions, from one state to the other. Hydrogen chloride and stannic chloride, for example, in the pure state or in presence of non-ionizing solvents such as the hydrocarbons, behave as covalent compounds; but in water they are both ionized. The two states can even co-exist in the same solution; a weak acid such as acetic when dissolved in water behaves as a mixture of a covalent (non-ionized) substance with a small proportion of an ionized substance. This does not, however, settle the question at issue, which is: whether such substances undergo a definite change from one state to the other (or the two forms exist in equilibrium), or whether each molecule exists in a state intermediate between the two.

[9a] A rough estimate of the moment of the alkaline halides, of about 10×10^{-18} E.S.U., was made by Wrede, by the beam method. See Chapter V, p. 135.

[10] It is noteworthy that molecules of the type $A''' B'''$ are always covalent.

[11] See further *Z. Elektrochem.*, 34, 426–522 (1928).

It should ultimately be possible to decide the question by the methods of wave mechanics; and although that branch of physics has not yet developed far enough to give a complete answer, it has already thrown a good deal of light on the problem. The methods of calculation adopted will not be dealt with here, but the more important conclusions and the assumptions on which they are based may be stated as simply as the subject admits of.

The application of wave mechanics to the shared electron was originated by Hund, but most of the work has been done by London.[12] The concept of shared electrons put forward by G. N. Lewis in 1916,[13] which proved so fruitful in explaining the formulas of non-ionized molecules, had no real foundation in the older theory of atomic structure. The possibility of shared orbits enclosing two nuclei was not precluded by the Bohr theory, but that theory could not predict how such an orbit would behave, and so was unable to decide whether the change from an electrovalent to a covalent link was gradual or sudden.

[12] W. Heitler and F. London, *Z. Physik*, 44, 455 (1927) (H_2); London, *ibid.*, 46, 455 (1928); 50, 24 (1928); *Sommerfeld Festschrift* (Leipzig, 1928), p. 104; *Quantentheorie und Chemie* (Leipzig, 1928), p. 59; *Z. Elektrochem.*, 35, 552 (1929); *Z. Physik*, 63, 245 (1930). A general account of the conclusions is given by London in *Naturwissenschaften*, 17, 516–529 (1929). A very clear description of the fundamental assumptions and of the chemical bearings of the results is given by C. N. Hinshelwood in the *Annual Reports . . . of the Chemical Society*, 27, 11–18 (London, 1931).

[13] G. N. Lewis, *J. Am. Chem. Soc.*, 38, 762 (1916).

It is therefore satisfactory to those of us who have maintained throughout that there is a real distinction between these modes of union, to find that the modern developments of wave mechanics have completely justified our view. It is now recognized, on purely physical grounds, that there are two kinds of forces which can hold two atoms together in a molecule: the Coulomb force between oppositely charged particles, which was the force considered by Kossel, and another force not deducible from classical mechanics even with the aid of the quantum restriction, which approaches in character very closely to the original ideas of Lewis. It is not indeed impossible that there should be molecules in which both of these forces are operative at the same time between the same two atoms; but it can be shown that this will rarely happen, and that in the great majority of instances the force uniting two atoms is practically entirely either of one kind or of the other. As London says:[14] "Between the two possibilities there is an intermediate range in which a transition between homeopolar [covalent] and heteropolar [electrovalent] linkage occurs. . . . It can be shown that this transition range is relatively small, and that the extreme cases of purely homeopolar or purely heteropolar links greatly predominate." It is not possible here to give a detailed account of the argument by which the existence of the second force was established, but the general conclusions can be stated.

If two neutral atoms, say two hydrogen atoms, approach one another, their electrons must begin to affect one another even at a considerable distance,[15] by a kind of resonance effect. The sense of the force will differ according as the orbits in question are symmetrical or antisymmetrical.[16] If they are antisymmetrical it will be a repulsion; but if they are symmetrical it can lead to an attraction. The relation thus set up between the two orbits, one belonging initially to each of the two atoms concerned, is subject to the Pauli prohibition, which demands that the orbits must differ in at least one quantum number; and the only one in which they can differ is the electron spin, which is initially undefined. The two orbits must therefore have positive and negative spins respectively. This means that each orbit will, so to speak, exercise the Pauli prohibition for both of the atoms concerned. For example, an isolated hydrogen atom can carry two electrons, as it does in the negative hydrogen ion, H^-; each of these is in a 1_1 orbit, one having a positive and the other a negative spin. But if a neutral hydrogen atom, whose single electron has, say, a positive spin, forms a covalent link with a second neutral hydrogen atom, not only must the electron of the second atom have a negative spin, but when the relation is established neither atom has room for another electron in the first quantum group. This obviously corresponds exactly to the mechanism assumed by Lewis. The link consists in a relation established between two electrons, which explains what was previously very mysterious, why two electrons are necessary to it; and when it is established, each of the electrons "counts" for both atoms; each of them fills, or at any rate prevents any other electron from filling, one place on each atom. It follows that every unpaired electron in an atom—every electron which has not already got a fellow in the same orbit in the atom but with an opposite spin—can form a link with another atom which has a similar unpaired electron. The formation of the link pairs these electrons with one another and so prevents either of them from forming a further link with any other atom. This exactly corresponds with the chemical experience that the formation of a link between two atoms uses up one unit of combining power for each of them.

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[14] London, *Naturwissenschaften*, 17, 525 (1929).

[15] It must be remembered that in wave mechanics the electrical density around an atom is not sharply defined, as in the Bohr theory, but extends indefinitely into space with diminishing intensity.

[16] "A function is called antisymmetrical when if its variables are exchanged its sign is reversed"—London.

These conclusions can be expressed on a model in wave mechanics only by giving the distribution of electrical density round the atoms. This has been done for the hydrogen molecule and the results are given by London.[17] Speaking roughly, we may say that whereas the electronic orbits of two electrovalently linked atoms are separate from one another, those of two covalently linked atoms interpenetrate.

[17] See diagram in London, *Naturwissenschaften*, 17, 522 (1929).

The magnitude of the forces which arise in this way—the energy of formation of covalent links—cannot yet be calculated in any detail, except for the simplest systems. For the hydrogen molecule, however, it has been shown to give as the energy of dissociation 3.2 volts, and as the distance between the two nuclei 0.80 Å,[18] results in reasonable agreement with the observed values of 3.8 volts and 0.75 Å.[19]

But although the absolute magnitude of the force cannot usually be calculated, we learn a very important fact about its variation with the distance between the atoms. This can be shown to be exponential, so that it must diminish very rapidly as the distance increases. On the other hand the Coulomb force between ions—the electrostatic attraction—falls off of course as the inverse square of the distance, and therefore much more slowly.[20] This enables us to construct a diagram (although we cannot yet put in the numerical values) showing the variation, with change of distance between the nuclei, of the magnitude

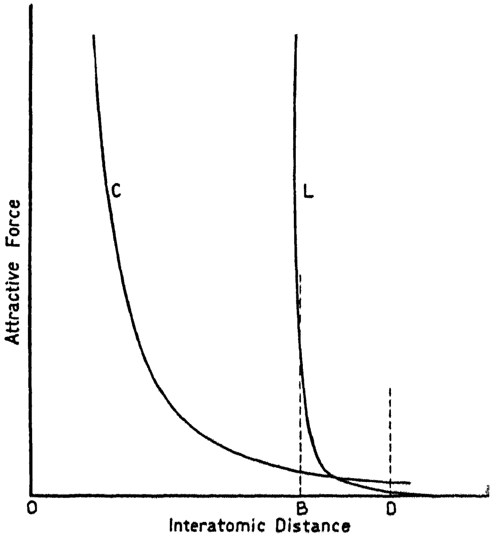

FIG. 3

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[18] London, *ibid.*, 519.

[19] S. C. Wang, *Phys. Rev.*, 31, 579 (1928).

[20] "Im übrigen ist zu bemerken, dass die wie e^{-R} abfallenden homöopolen Wirkungen eine viel geringere Reichweite haben als die mit einer Potenz von $1/R$ abfallenden Polarisationswirkungen."—London, *Z. Elektrochem.*, 35, 555 (1929).

of the forces involved in the formation of a link of either kind. This is given in Figure 3, where the curve *C* represents the electrostatic (Kossel or Coulomb) force, and *L* the covalent force of London and Lewis. In the actual formation of the molecule, the approach of the atoms will be stopped at some point, owing to a third, repulsive force which is due to the resistance of the electronic orbits generally to distortion and the repulsion of the nuclei; this force changes still more rapidly with the distance, and so is perceptible only at very short distances. The repulsive will be equal to the attractive force for some value of *d*, which will be the distance between the nuclei in the molecule; but as the values are not determined we cannot say what this distance will be. It is obvious, however, from the shape of the *C* and *L* curves and the angle at which they cut one another, that the range of distances over which both of these forces are operative to a comparable extent is very small, being limited to a small distance on either side of the point of intersection, say between the points *B* and *D* on the diagram. The resistance of the atom to deformation may stop the approach at any point. If this point lies to the right of *D*, the link will be (practically) wholly due to the electrostatic force, and therefore electrovalent; if it lies to the left of *B* it will be (practically) wholly covalent. Only if the point happens to lie within the small range *B–D* will the resultant be of a mixed character; and since this distance is small, the formation of such a mixed link is not likely to be of frequent occurrence. This conclusion is entirely supported by the experimental evidence, as shown on page 51.

The case however is really stronger than this. The alternatives we have to consider are not whether the force between two charged ions is electrovalent or covalent, which is what the diagram indicates. The question is whether two atoms which combine will ionize in doing so or not. The covalent London force can act of course whether they are neutral atoms or ions; but the Coulomb force vanishes if they are neutral.[21] Thus the answer which wave mechanics gives to the question whether there is an essential distinction between electrovalent and covalent links is this: There are two kinds of attractive forces possible between atoms, which we may call electrovalent and covalent. The second can exist whether the atoms are charged (ionized) or not; the first only when they are charged. The theory can thus account for linkages between uncharged atoms, and in these the Kossel (Coulomb) force is absent, apart from a small effect due to polarization. When the atoms are charged it is possible that both the Coulomb and the London forces may play an appreciable part in their linkage, but this is not likely to occur often.

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[21] This statement needs some modification in view of the mutual polarization of the atoms on close approach (van der Waals force), which will cause even neutral atoms to exert an electrostatic force on one another; but the argument remains essentially valid.

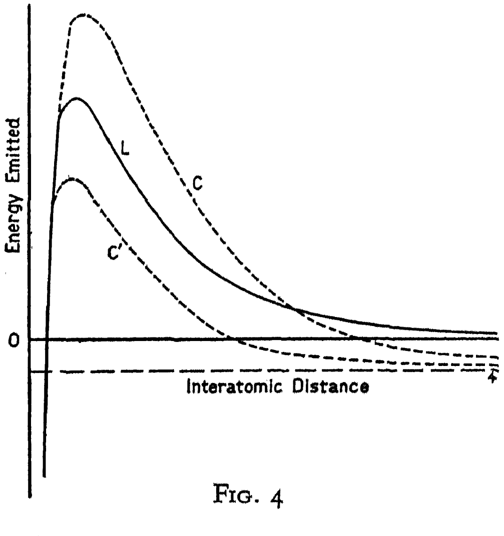

FIG. 4

Whether the atoms in any particular molecule are electrovalently or covalently linked will depend on the amount of energy evolved in forming the two kinds of link. The general relations are shown in Figure 4. The ordinates give the energy emitted when one atom is brought from infinity to distances from the other represented by the abscissae. The curve *L* is for uncharged atoms (London force), *C* and *C′* are two possible curves for the Coulomb force. For these latter we have to take account of the energy change involved in converting the original neutral atoms into a positive and a negative ion. This always entails the absorption of energy,[22] and hence the C and C' curves must start from a lower base line than L. The approach of the atoms, as we have seen, is resisted at close quarters by the repulsion due to the deformation of the orbits, so that the curves pass through a maximum and ultimately become negative for very close approach.

The atoms obviously will continue to approach one another as long as this evolves energy, and thus the maximum of the curve gives, for each particular kind of linkage, the distance between the linked atoms and the energy of formation of the link. Which form of linkage—whether between uncharged or ionized atoms—is effected will depend solely on the relative values of the energy evolved by each. If C is the curve for the atoms in question in the ionized state, then, since its maximum is higher than that of L, we shall get an electrovalent link; if the ionic curve is C', which has a lower maximum than L, the link will be covalent.

From the way in which the two curves cross each other, and because the ionic state represents separate and the covalent interpenetrating electron atmospheres, we should expect the atoms to be nearer together in covalent compounds than in salts. We can test this experimentally by comparing for a series of compounds the interatomic distances found by Goldschmidt[23] in the covalent crystals, with the sum of the radii of the same atoms in the ionized state as determined in their salts. It will be seen from Table IX that the theoretical anticipations are fulfilled.

London has also investigated the question of the maximum number of covalences that an atom can form. His work so far covers only the elements of the first short

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[22] Two isolated atoms can be converted into a cation and an anion (an electron being transferred from one to the other) only by the expenditure of energy. Even in the most favorable case of an alkali metal, which ionizes very readily, and a halogen atom, which has a large electron affinity, the work required to ionize the metal is greater than that gained by adding the electron to the halogen, if the atoms are assumed to be far apart; with potassium and chlorine the difference is about 0.5 volt (about 12 kgm-cal per gram-molecule). The large quantity of heat produced when potassium and chlorine combine is due to the energy evolved by this pair of ions when they come together owing to the Coulomb attraction, to form the salt. The energy needed to ionize the atoms is all recovered by the time the ions have approached within 29 Å of one another; the further energy evolved when this distance is reduced, as it ultimately is, to about 3 Å gives the heat of formation of potassium chloride from its constituent neutral atoms.

[23] See Chapter III.

TABLE IX

Compound	Sum of ionic radii	Dist. in covalent crystal	Difference	
			Ångström	Per cen
BeO	1.66	1.645	0.015	0.91
MgTe	2.81	2.76	0.05	1.8
ZnS	2.57	2.37	0.20	8.4
ZnSe	2.74	2.45	0.29	11.8
ZnTe	2.86	2.64	0.22	8.3
CdTe	3.06	2.80	0.26	9.3
AgI	3.33	2.81	0.52	18.6

period (Li–F). Here he finds that the maximum is 4; this must obviously be so if we suppose that, as will normally be the case, the electrons paired in the covalences are all in the second quantum group, since this group is limited to 8, and his system implies that for every valence electron utilized a second place in the group is occupied. He further finds that this limitation to 4 does not hold for elements in the second short period (Na–Cl). His conclusions so far as they go are in accordance with the covalence rule.[24] He has not yet carried his analysis further in this direction, and indeed has recently been occupied rather in strengthening the foundations of his theory. When London comes to examine the behavior of the heavier elements it will be very interesting to see whether he finds the limit in the second short period to be 6, as the chemical evidence clearly indicates, or 9, which is the value one would expect his method to give, since the maximum number of electrons in the third quantum group is 18.

A point arising out of this work is the covalence maximum for hydrogen. On the chemical evidence it must be admitted that hydrogen can form two covalent links, one of course by co-ordination. If we accept the Lewis theory, now supported by wave mechanics, the hydrogen atom in this condition must have 4 shared electrons. It has been stated that this is forbidden by the Pauli prohibition. Now the Pauli prohibition leaves this matter exactly where it was in the original Bohr theory. On that theory no atom can have more than 2 electrons in the first quantum group. London's theory of sharing may be said to have made some difference, inasmuch as it shows that, from the point of view of the maximum size of a quantum group, shared electrons must be treated on the same basis as unshared, which on the Bohr theory could not be proved, although it was generally assumed. It was always recognized that, so far as shared electrons could be regarded as forming part of the normal quantum groups, a co-ordinated hydrogen atom could have only two electrons in the first quantum group and must have the other two in the second. There is nothing in the London theory[25] or in the Pauli rules to make this impossible. On the London theory the process of co-ordination must be regarded as a double one: an electron is first transferred from the donor to the acceptor, and then the London relation is established between this electron and one unpaired electron in the donor. When the acceptor is a hydrogen atom that has already formed one covalent link in the normal manner, and so has its first quantum group complete, the transferred electron must go to the second quantum group.

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[24] See Sidgwick, *Electronic Theory of Valency* (1927), p. 152.

Thus the physical theory indicates that in the majority of instances the atomic link will be maintained practically only by one or by the other of the two kinds of force, and that links in which both kinds play any considerable part will at any rate be rare. This conclusion is supported by a series of arguments on the experimental side, which indicate that there is in practice a clear distinction between the two kinds of link, and a sharp change of properties when we pass from compounds of one kind to those of the other. These may be briefly enumerated and discussed.

(1) The covalence rule, which is based on chemical evidence—on the examination of the structures of known compounds—and is supported as we have seen by the theoretical investigations of London so far as they have gone, indicates that the number of covalent links which an atom can form is limited in accordance with its period in the Periodic Table, but no such limit is imposed on its electrovalence. For example, the limit in the first short period is four; but this is compatible with electrovalences of -1, 0, and $+1$ in $[BF_4]^-$, CH_4, and $[NH_4]^+$. This would

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[25] In his discussion in *Naturwissenschaften*, 17 (1929), London says (p. 523): "Wir sehen von solchen Atomzuständen ab, welche aus dem Grundzustande nur durch Anregung der Hauptquantenzahl zu erreichen sind."

seem to show that the two kinds of link have quite a different relation to the structure of the atom.

(2) The evidence of the dipole moments, as we have seen, is in favor of this view; it indicates that the ionic deformation does not diminish the moment of the link by more than some 20 per cent, while the covalent link reduces it by at least 80 per cent.

(3) Further evidence is given by the sharp distinction between salts and non-salts in volatility, solubility, and electrical conductivity. Thus the halides of an element are either salts with high boiling points falling relatively slowly as the atomic weight of the halogen increases, or they have low boiling points which rise rapidly with this increase. As examples, compare the boiling points: $NaF = 1695°$, $NaI = 1300°$, a fall of 20 per cent; $SiF_4 = -90°$, $SiI_4 = +290°$, a rise of 200 per cent. A particularly instructive fact is that if we take an element which in its general properties is intermediate between the metals and the non-metals, and which therefore might be expected to give, if anything could, halides which are intermediate in character between salts and non-salts, we find that this does not happen. Its fluoride behaves as a salt with a high boiling point, while its other halides conform closely in behavior to the typical non-salts.[26] This is illustrated by the halides of sodium, silicon, aluminum,[27] and tin, the boiling points of which are given in Table X and plotted in Figure 5.

TABLE X

Boiling Points of Halides of Sodium, Silicon, Aluminum and Tin, at 760 mm.

NaF	$NaCl$	$NaBr$	NaI
1695°	1441°	1393°	1300°
SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
−90°	+57°	153°	ca. 290°
AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
ca. 800°	183°	260°	350°
SnF_4	$SnCl_4$	$SnBr_4$	SnI_4
705°	114°	203°	300°

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[26] The exceptional position of fluorine is in accordance with the Fajans theory.

[27] The fact that the non-salt halides of aluminum have higher boiling points than those of tin is of course due to their polymerization in the vapor.

In electrical conductivity again Biltz has shown[28] that at their melting points all the chlorides of the elements with only two or three exceptions give values which are either greater than 10^{-1} or less than 10^{-7}.

There are also, as we have seen, certain halides which in some conditions behave as salts, and in others as non-salts, such as stannic chloride and hydrogen chloride. If electrovalence and covalence are only the extremes of a continuous series of states, we should expect these compounds to be in an intermediate state and to have properties on the line between those typical of the two classes. But we do not find this at all: on the contrary such compounds when they behave as salts, for example, in water, behave as 'good' salts, and when they are covalent, as in the pure state, have the full covalent character.

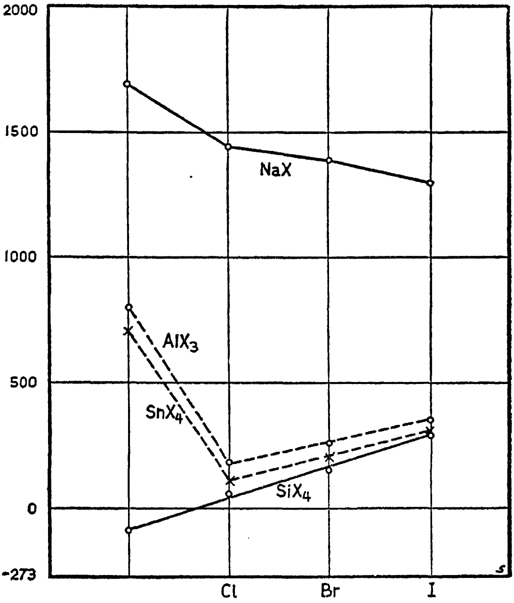

FIG. 5

(4) Another line of evidence, of enormous range, is that provided by organic chemistry, that covalent links

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[28] Biltz, *Z. anorg. allgem. Chem.*, 133, 312 (1924). Biltz and Klemm, *ibidem*, 152, 267 (1926). See also Sidgwick, *Electronic Theory of Valency*, p. 105.

are directed in space, while electrovalent are not. This was pointed out by Meisenheimer[29] in 1908, in a discussion of the amine-oxides and the ammonium compounds. He showed that their behavior indicated that four of the groups attached to a pentavalent nitrogen atom retained their relative positions, and if they were all different could give rise to optical antimerism; while the fifth group, which was ionized, had a wholly different relation to the molecule, and its position was uniquely determined by the other groups present. This distinction between the two different kinds of link is exemplified by many other results of organic chemistry, by the evidence for the absence of free rotation in doubly linked compounds—if the double link is only a double electrostatic attraction there is no reason why it should not allow of rotation of the attached atoms—and by the way in which a complicated organic skeleton, such as that of an alkaloid, retains its form through an elaborate multiplicity of reactions. If the covalent link is only an ionized link with a small dissociation constant, all organic isomers must ultimately go over into the most stable form.

A more delicate proof of this is given by Hevesy's work[30] on radioactive indicators. If a salt of radioactive lead (*i.e.* lead containing a little of a radioactive isotope) is mixed with an inactive lead compound (*e.g.* inactive lead nitrate and active lead chloride) and the two are separated after solution, then if the second compound was ionized as well as the first the activity will become equally divided between the two. But if one of the compounds is not ionized then its lead atoms retain their attached groups throughout, and after separation the activity is found to be still confined to the compound which originally possessed it. Owing to the rapidity with which ionization and de-ionization take place—the velocity being too great to be measured, as we know from the behavior of weak electrolytes like acetic acid—this test is very delicate, and even a minute degree of ionization is enough to secure a uniform distribution of the activity in a short time; this occurs for instance with lead tetraacetate which is almost wholly in the covalent form, and where no other test will detect the presence of quadrivalent lead ions. But with a compound like lead tetraphenyl no redistribution occurs, showing that there is no ionization.

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[29] Meisenheimer, *Ber.*, 41, 3966 (1908).

[30] G. von Hevesy and Zechmeister, *Ber.*, 53, 410 (1920); *Z. Elektrochem.*, 26, 151 (1920). See also Paneth, *Radio-Elements as Indicators* (This SERIES, v. 2, New York, 1928), p. 47f.

(5) Another line of evidence is derived from the X-ray examination of crystal structure, which shows that crystal lattices can be divided into two classes, the ionic and the molecular. This will be discussed further in the next chapter, but some of the more striking examples may be quoted here. Grimm and Sommerfeld[31] have shown that crystals of the composition *AB* (such as NaCl, CSi) form four types of lattice. Two of these, the CsCl (8:1) and the NaCl (6:1) lattices, are close-packed and these are found to be given by compounds which in other ways behave as salts. The other two, the diamond and the wurtzite lattices, both 4:1, and both very similar, which are not close-packed, occur with compounds for which Fajans' theory leads us to expect high deformation. The difference in closeness of packing is exactly what should occur if in the former (salts) the attraction is electrostatic and so not directed, while in the latter it is directed owing to the interpenetration of the electronic atmospheres. That the valence forces really are electrostatic in one type but not in the other is strongly supported by a discovery by Goldschmidt.[32] He showed, as has already been mentioned, that if we compare two compounds *A′B′* and *A″B″* (where *A′* and *A″* belong to the same period, and also *B′* and *B″*) the interatomic distance is from 8 to 10 per cent less for the divalent elements than for the univalent, as is illustrated in Table XI.

TABLE XI

NaF	2.310	KCl	3.139	RbI	3.663Å
MgO	2.104	CaS	2.843	SrTe	3.324
Diff.	0.206		0.296		0.339
% Diff.	8.9		9.4		9.3

This is to be expected, since the double charge crushes the atoms together more. If, on the other hand, we make a similar comparison between compounds with lattices of the 4:1 type, the valence of the ions has practically no effect, the distances seldom varying by 1 per cent over the whole range of valences from 1 to 4 (See Table XII). This again is to be expected if the bond here is not the electrostatic charge, but the sharing of electrons.

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[31] Grimm and Sommerfeld, *Z. Physik*, 36, 36 (1926).
[32] Goldschmidt, *Z. Elektrochem.*, 34, 459 (1928).

TABLE XII

	AgI	CdTe	InSb	SnSn
Dist.	2.811	2.799	2.793	2.79Å

Other examples of the light thrown by crystal structure on the nature of the atomic linkage are given in Chapter III.

(6) Another distinction between covalent and electrovalent links, which likewise indicates a perfectly sharp division, has been established by Franck and his pupils.[33] This depends on the dissociation of the molecules by light. When light is passed through a polyatomic gas it gives a band spectrum, each band consisting of a series of regularly spaced lines, due to the absorption by the molecule of successive quanta of oscillational energy. At a certain point towards the violet, these lines are replaced by a range of continuous absorption. This means that when the molecule has absorbed a certain amount of oscillational energy its atoms separate from one another and the molecule is dissociated. When this happens, the absorption of individual oscillational quanta—and hence the line series—ceases; the molecule can absorb all the shorter wave-lengths, because the extra energy beyond that required for dissociation is transformed into kinetic energy of the products of dissociation, which fly apart with increasing velocity. Thus the beginning of the continuous absorption gives us the wave-length and therefore the energy of the light which is just sufficient to dissociate the molecule. Now the heat of dissociation of a gas can often be determined in another way, by observing the change of the amount of dissociation with

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[33] Franck, Kuhn and Rollefson, *Z. Physik*, 43, 155 (1927); Sponer, *Z. Elektrochem.*, 34, 483 (1928).

temperature. We may take iodine as an example. Its thermal dissociation, which is known to break up the molecule into two neutral atoms (not ions), indicates that the heat of dissociation is 34.5 kgm-cal per gram-molecule. On the other hand the energy corresponding to the beginning of the continuous absorption in the spectrum is found to be 56.7 kgm-cal. It is therefore clear that the photodissociation gives rise to atoms having more energy by about 22 kgm-cal than the normal neutral atoms. It can be shown that they are not ionized, and so one or both of them must be excited, that is, in a higher quantum state than the normal. The atomic spectrum of iodine shows that the first stage of excitement, the smallest quantum jump, corresponds to an energy of 21.5 kgm-cal per gram-atom. Since 34.5 (heat of thermal dissociation) + 21.5 (excitement of one atom) $=56.0$, and the observed energy of photodissociation is 56.7, it is clear that the iodine molecule I_2 is dissociated by light into two neutral atoms, one of them excited.

On the other hand if a definite salt molecule, such as sodium chloride, is exposed to radiation, we find the same phenomenon of a series of lines followed by continuous absorption, but the point where the latter begins shows that the energy of photodissociation is that required to break up the molecule into two neutral unexcited atoms. That they should be neutral atoms is perhaps at first sight surprising, as we might have expected that the atoms which were ionized before dissociation would remain so afterwards; it is easier to understand when we realize[34] that the conversion of dissociated ions into neutral atoms is an exothermic change.

The behavior of covalent molecules like iodine, where one of the resulting atoms appears with an electron in the next higher quantum state, is no doubt to be explained ultimately by the mechanism of the tearing away, so to speak, of the shared electron.

It is thus clear that the dissociation of a molecule by radiation can occur in two ways; the products are always neutral atoms and not ions, but if the link is electrovalent the products are normal (unexcited) atoms, whereas if it is covalent one of the atoms is excited.

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[34] See note page 49.

This gives us a sharp distinction between the two types of linkage. All the molecules so far examined have given quite unambiguous results, and show that their linkage is either of one kind or of the other. Examples of molecules dissociating in the first way, into two neutral atoms, one excited, are: Cl_2, Br_2, I_2, O_2, H_2 and S_2. The second kind of dissociation, into two neutral unexcited atoms, is shown by NaCl, NaI, KBr and RbBr. These are, of course, typical representatives of the two classes of compounds, and we should expect them to differ sharply in behavior.[35] It is more interesting to consider the results obtained with molecules whose character is less obvious. The number of these which have so far been examined is not large, but it includes two important groups, the halogen compounds of hydrogen and of silver.

The halogen hydrides, from their undoubted high ionization in water, were for a long time supposed to be ionized even in the gas, in spite of this gas having all the ordinary characteristics of a covalent substance. Now, however, it has been shown[36] that the photodissociation of hydrogen iodide leads to the formation of a normal hydrogen and an excited iodine atom. Similar results have been obtained for hydrogen bromide, and no doubt the chloride behaves in the same way.

As regards the silver halides, the evidence of crystal structure shows that while cuprous chloride, bromide and iodide are all of the diamond type, and hence must have molecular (covalent) lattices, silver chloride and bromide have a sodium-chloride lattice and so are ionized in the solid; and silver iodide crystallizes in two forms, of which one is ionic and the other not. This agrees with the simple Fajans theory. The copper and silver ions, being much smaller than those of the alkalies, are more likely to deform the anions up to the point of forming a covalence; of

[35] The results are important as showing that the alkaline halides are ionized not only in the solid but also in the gaseous state.

[36] For references, see Sponer, *Z. Elektrochem.*, 34, 487 (1928).

the two copper, being the smaller, should have more deforming power; while of the halogens, iodine is the most deformable and so the most likely to become covalent. Thus the facts observed for the crystals:

	Cl	Br	
Cu′	covalent	covalent	covalent
Ag	ionic	ionic	covalent ionic

are a good exemplification of the theory.

This, however, applies only to the crystalline state. In the vapor the deformation may proceed further, because each cation is affecting only one anion, and as these substances are on or near the line where deformation passes over into covalence, it might well happen that the extra deformation in the vapor was enough to make the molecule cross this line. Accordingly we find that silver chloride is dissociated by radiation into a normal (neutral) chlorine atom and an excited (neutral) silver. The same thing occurs with the bromide and iodide. Thus while all three give ionic lattices, and all but the iodide only ionic lattices, all three form covalent molecules in the vapor. If the difference had been in the other direction, a covalent crystal giving an ionized vapor, it would have been inexplicable.

The photodissociation thus gives us another criterion, which separates molecules sharply into two classes, covalent and ionized.

(7) A detailed study of the results obtained by Fajans for the deformation of ions also gives proof that the covalent link is essentially distinct from the electrovalent. The beautiful regularities which he observes with the less distorting elements of the A sub-groups, and the clear relations he establishes among these elements between the size of the cation and its deforming power,[37] no longer hold when we come to the elements of the B sub-groups (for example, zinc, cadmium, and mercury) with their greater power of deformation. The results are then much less regular; indeed Fajans expressly points out that here we have to assume specific differences between different cations which are not directly related to their size. It is

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[37] See Figures 1 and 2, pp. 34, 37.

evident that as long as he is dealing with ionized molecules—and his compounds of the A elements are nearly all of the ionized type—the problem is simple. But with the B elements the results are complicated by the appearance of a new set of phenomena, those of covalence.

(8) The same conclusion emerges equally clearly from the calculations by Born, Landé, Heisenberg, and others,[38] of the lattice energies and theoretical heats of formation of compounds. These are founded on an ionic conception of atomic linkage, but they take account of the deformation of the ions, and should therefore be applicable to all molecules if all molecules are essentially ionic. They enable us to calculate approximately the heats of formation of all compounds known and unknown; these heats should have a positive value for compounds which exist, and a negative for those which do not exist. If we confine our attention to existing compounds, we find that so long as these are salts the calculations give the expected results; but when we come to non-salts the calculated heats have no relation to the stability of the actual compounds, and molecules which are really very stable appear to be highly endothermic. Thus, to take only the chlorides of the elements of the two short periods, LiCl, NaCl, $MgCl_2$, and $AlCl_3$ are all found to be exothermic, as of course they should be. But the heats of formation of $BeCl_2$, BCl_3, CCl_4, and FCl are found to be practically zero, and those of $SiCl_4$, PCl_3, and Cl_2 to be highly negative. It is evident that the conception of ionic linkage is applicable to the first of these classes of compounds, but not to the rest.

Thus a series of quite different lines of argument based on experiment all go to show that there are two possible forms of linkage between the atoms in a molecule, and that the two can in practice be sharply distinguished. When we combine these results with the conclusions of wave mechanics, we see that they are in complete agreement with the theoretical deduction that two kinds of forces are possible between atoms; and that they strongly support the conclusion, which the mathematical theory renders probable but in its present form does not prove, that any actual link between atoms is due practically only to one, or to the other of these forces, and that links in which both kinds play any considerable part—links which are truly intermediate between an electrovalence and a covalence—rarely if ever occur.[39] The controversy as to the distinctness of electrovalent and covalent links has been going on as long as there has been any electronic theory of valency at all, and the experimental evidence has always seemed to be in favor of the distinctness. But the question could not be settled until the physical theory was developed, and when this development came it proceeded entirely along the lines of assuming a gradual change, and appeared to suggest that one form must pass over into the other by a continuous series of stages. It is now clear that these conclusions are not incompatible. With a continuous change of one parameter, the interatomic distance, there is a continuous change from a state in which the electrovalence predominates to that in which the covalent force predominates. But the shapes of the curves are such that the chances are strongly against the two forces in any particular link being of comparable magnitude—against the link being really mixed; and the experimental evidence shows that in fact the great majority of links, and perhaps all, can be classified as being due to one or to the other force, and not to both.

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[38] For a short account of the methods and their results, see E. Rabinowitsch and E. Thilo, *Periodisches System* (Stuttgart, 1930), pp. 271–282.

[39] At the same time the possibility of such links being occasionally found should not be overlooked.

CHAPTER III

DIMENSIONS OF COVALENT LINKS

HAVING seen what are the conditions which lead to the formation of covalent links, we can now consider these links in more detail. G. N. Lewis has said, with some justification, that covalent links are the only true links in chemistry. The attachment between ions—the electrovalent bond—is essentially not between atoms as such, except where the ions happen to be monatomic, but between the charged molecules which as wholes constitute the ions. The strength of the link, its direction, and the distances between the ions, all are dependent on the particular circumstances of the salt. The covalent link, on the other hand, is a real attachment or junction between specified ions. The linking electrons form part of both of them, and the linkage involves definite physical properties, dependent no doubt to some extent on the physical surroundings of the molecule, but primarily determined by the nature of the linked atoms. Our object is to discuss some of the more important of these physical properties, and the methods by which they can be investigated.

Of the properties of covalent links some concern one link only, and others have to do with the relation of several links of the same atom to one another. The most obvious of the properties of an individual link is its length, the distance between the nuclei of the two linked atoms. The next is its strength, the work required to bend it or to stretch it, or to break it entirely, this last being the same thing as the energy given out in its formation. Then we have the question of the proportion in which the linking electrons are shared between the two atoms, the electrical dipole moment of the link. These questions will be discussed in this and the next two chapters. In Chapter

VI I shall consider one of the most important of the relations between two links of the same atom, the angle between them; this is the subject generally known as stereochemistry, but recent developments have shown that in dealing with it the limited methods of organic chemistry can be supplemented by the evidence from a whole series of physical determinations. Many other properties of the covalent link might be enumerated: the polarizability of the molecule, which depends on the linkage of its component atoms, determines the refractive power and the volatility of the compounds; the state of the electronic orbits affects the magnetic behavior. The list might be continued indefinitely, but it seems better in this book to deal with a small number of the more important properties in detail.

There is one general difficulty which arises in the investigation of any property of a specified link A–B. Most links are found not alone but only in conjunction with other links in polyatomic molecules. Even if we are able to examine a molecule A–B that contains only the link in question, the information which we gain is of limited value, except in so far as it can be extended to the behavior of this link in more complicated molecules. We can therefore make little progress unless we can assume as a first approximation that the properties of a link are unaffected by the other links present in the same molecule. This assumption is certainly not strictly true; indeed we may expect that our most valuable information as to the relations between structure and behavior will be derived from a study of the influence of links on one another. But as a first approximation the assumption can be shown experimentally to be legitimate. We must not make use of it, however, in examining any property without inquiring into the evidence for its validity as applied to that particular property.

The present chapter deals with the length of the covalent link, the methods by which it can be determined, and the results to which they lead.

This question is often stated in a different way, in terms of the sizes of the constituent atoms. But the more the subject is studied, the less definite does this idea of absolute atomic size appear. So long as the atoms were regarded as rigid structures the matter seemed simple; it was only necessary to ascertain their radii, and the problem was solved. But as Debye[1] says: "the time when it was allowable to play with molecules as if they were hard billiard balls is past." It is very difficult, and the difficulty is immensely increased by the new conceptions of wave mechanics,[2] to say exactly what we mean by the "outside" of an atom. If as is probable, the electronic atmospheres of two covalently linked atoms interpenetrate, the sum of their radii must be greater than the distance between their nuclei. These difficulties are not only great, but from our point of view they are unnecessary. The definition of the size of the link as the distance between the nuclei of the two atoms is quite unambiguous, and this distance can be measured by various physical methods.[3] At the same time we obviously want if possible to get an idea of the contribution of each atom to the link, and the simplest way would be to regard the distance as made up additively of two parts, one depending on each atom. The experimental evidence indicates that this is justifiable, and that with certain limitations the additive law holds; in other words, that as long as the links are similar, their length is the sum of two distances, one for each atom.[4] The phrase "atomic radius" will be used in this sense, as meaning, not the true radius of the atom, whatever that may be, but the "effective" radius, the contribution which each atom may be regarded as making to the length of the link.

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[1] Debye, *Schweiz. Naturf. Ges.*, 2, 128 (1926).

[2] For a calculation of the true atomic radii on the principles of wave mechanics see L. Pauling, *J. Am. Chem. Soc.*, 49, 765 (1927); *Proc. Roy. Soc. London*, A-114, 181 (1927).

[3] The volume occupied by a molecule can, of course, be found by dividing the molecular volume by the Avogadro number (the number of molecules in a gram-molecule). But this quantity is of little value, because it takes no account of the geometrical properties of the crystal; a great advance was made when W. L. Bragg suggested—*Phil. Mag.*, [6] 40, 177 (1920)—the calculation of the "atomic radii" from the distances between the atoms in the crystal as determined by X-ray analysis. Later work has shown, as we have already seen, that his original values are subject to modifications, but they pointed the way which has led to important developments.

[4] The question of the way in which the nature of the link affects the "radius" of the atom, is one of great importance, and will be discussed later.

METHODS OF MEASURING LINKS

The methods by which the length of a link can be measured fall into three classes, according to the agent employed, which may be X-ray or visible or infra-red radiation or lastly, though this method is only beginning to be developed, cathode rays.

X-ray Methods

The most familiar application of X-rays is to the determination of crystal structure.[5] The power which the electrons of an atom have of scattering X-rays enables the crystal to be used as a grating,[6] since the interatomic distances are of the same order of magnitude as the wave-lengths of these rays. The spacing of the grating can thus be measured if the wave-length is known. A compound will give several series of lines of different intensity, depending on the scattering power of its various atoms. The measurements can be made with accuracy, and if the arrangement of the atoms in the molecule can be determined (alternative arrangements are sometimes possible), we can calculate from them the distances between pairs of atoms in the molecule.

This method has been extended by Debye and Scherrer[7] so that it can be used where it is not possible to obtain individual crystals of any size. Debye and Scherrer showed that when a narrow pencil of X-rays is sent through a mass of powdered crystals, those fragments which happen to be in the right position with respect to the beam will reflect the rays, and thus a series of rings is obtained from whose separation the spacing of the atoms can be determined.[8] An ingenious development, invented by Wyckoff and adopted widely by Goldschmidt, has proved of great service. This consists in mixing the powdered crystal with powdered sodium chloride; the rings of sodium chloride then appear on the same plate with those of the substance under investigation, and give a very simple and accurate method of calibration.[9]

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[5] For the details of the measurements see, for example: W. H. and W. L. Bragg, *X-rays and Crystal Structure*, 1925; R. W. G. Wyckoff, *The Structure of Crystals*, (Am. Chem. Soc. Monographs, No. 19, 1924; 2d ed. 1931).

[6] There is this difference from an optical grating, that the rays are not reflected wholly from the surface, but penetrate several layers deep into the crystal.

[7] P. Debye and P. Scherrer, *Nachr. Ges. Wiss. Göttingen Math-physik. Klasse*, 1916, 16; *Physik. Z.*, 17, 277 (1916). See also A. W. Hull, *Phys. Rev.*, 10, 661 (1917).

[8] They even extended this method to liquids—Debye and Scherrer, *loc. cit.*; see also C. Drucker, *Physik. Z.*, 29, 273 (1928)—but owing to the difficulties of interpretation mentioned in the next paragraph, this application has been but little used.

Quite recently Debye has been able to obtain X-ray interference figures from the molecules of a gas or vapor.[10] This is of exceptional importance. In the solid state the molecules are under some restraint and the distances between their atoms may therefore be modified. The results obtained with liquids are peculiarly difficult to interpret.[11] If, for example, the figures obtained with liquid carbon tetrachloride indicate a certain uniform distance between chlorine atoms, we cannot tell from the diagram whether these are atoms in the same molecule, or neighboring atoms in different molecules. With a gas this difficulty does not arise. On the other hand, the scattering power of the small quantity of material in a given volume of gas is minute compared with that of a solid or liquid, and great experimental difficulties had to be overcome before definite images could be obtained in a reasonable time. It has now been found possible to work with exposures of not more than 4 or 5 hours, and the results tell us the distances separating the atoms in the unconstrained gaseous molecule. The later work has shown that the calculation of the results in the form given in the earlier papers, in which the atoms were treated as points which caused scattering, is inaccurate. The scattering is really due to the electron orbits, and allowance must be made for this as well as for the Compton effect, which complicates the calculations. These mathematical difficulties have now been overcome, however, through the work of Heisenberg.

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[9] According to Goldschmidt, "Geochemische Verteilungsgesetze der Elemente" (Oslo 1927), VIII, p. 21, the accuracy of the lattice measurements by this method is within 0.05 to 0.1 per cent.

[10] P. Debye, L. Bewilogua, and F. Ehrhardt, *Physik. Z.*, 30, 84 (1929); *Ber. Verhandl. sächs. Akad. Wiss. Leipzig Math-phys. Klasse*, 81, 29 (1929); P. Debye, *Physik. Z.*, 30, 524 (1929); *idem*, 31, 142, 419 (1930); *Proc. Phys. Soc. London*, 42, 340 (1930); *Z. Elektrochem.*, 36, 612 (1930); the true values of the distances are those given in the last of these papers. See also L. Bewilogua, *Physik. Z.*, 32, 265 (1931); H. Mark, *Z. angew. Chem.*, 44, 125 (1931); H. Gazewski, *Physik. Z.*, 32, 219 (1931).

[11] For methods by which this difficulty may be overcome see P. Debye, *Physik. Z.*, 31, 348 (1930); P. Debye and H. Menke, *Physik. Z.*, 31, 797 (1930).

The corrected values for carbon tetrachloride, chloroform and methylene chloride are given in the last of the papers quoted above. Their bearing is discussed in Chapter VI, page 233. The method of Mark and Wierl is very similar to this, except that it uses electron rays in place of X-rays; it is discussed below (page 73) and a list of the results obtained by the two methods is given in Table XXI (page 89).

Measurements with Visible and Infra-red Radiations[13]

It is now recognized that band spectra—spectra consisting of a large number of closely spaced lines—are only produced by polyatomic molecules, and not by single atoms. Every line in a spectrum of course corresponds to a change in energy of the emitting or absorbing molecule, its frequency ν being related to the change from energy E_1 to energy E_2 by Bohr's equation

$$E_1 - E_2 = h\nu$$

where h is Planck's constant, 6.55×10^{-27} erg-second.[14] If the source of the line is an atom, the only possible energy changes are those in which one or more electrons jump to another quantum orbit, and these involve large amounts of energy, usually of the order of 1 to 10 volts, corresponding to between 12,000 and 1,200Å.[15] These electronic quantum

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[13] See Mecke, *Bandspektra* (Berlin, 1929); Cl. Schaefer and M. F. Matossi, *Das Ultrarote Spektrum* (Berlin, 1930).

[14] This is for an emission line where E_1, the energy before the change, is greater than E_2; for an absorption line E_2 is the energy before the change, and E_1 after.

[15] The phrase "an energy of 1 volt," or, as it is sometimes more accurately expressed, "1 electron-volt," is a current abbreviation for the energy acquired by an electron in falling through a potential drop of 1 volt, which is 1.591×10^{-12} erg; the energy is of course proportional to the voltage. Thus for 1 volt energy

$$h\nu = 1.591 \times 10^{-12}$$

$$= \frac{1.591 \times 10^{-12}}{6.55 \times 10^{-27}}$$

$$= 2.428 \times 10^{14}$$

Since the product of the frequency and the wave-length is equal to the velocity of light,

$$\text{wave-length} = \frac{2.9986 \times 10^{10}}{2.428 \times 10^{14}}$$

$$= 12{,}350\text{Å}$$

For an energy of V volts,

$$\text{Frequency} = 2.428 \times 10^{14} \times V$$

$$\text{Wave-length} = \frac{12{,}350}{V}\ \text{Å}$$

(*Continued on bottom of next page*)

jumps occur with polyatomic molecules as well, but in this case other changes are also possible, which are of two kinds.[16] The atoms in the molecule have a certain amount of energy of vibration or oscillation in the line joining them, and this can change by quanta each roughly of the order of 0.1 volt. Every electronic quantum change may be accompanied by the gain or loss of one or more of these vibrational quanta, and thus the spectrum contains a series of lines fairly evenly spaced at distances (for lines in the visible) of something like 300Å.[17] A series of still smaller energy steps is given by quantum changes in the rotational energy of the molecule round an axis perpendicular to the line joining the atoms; these are of the order of 0.001 volt and cause each of the vibrational lines to be

TABLE XIII

Conversion Factors for Absorption and Emission Spectra

Transition	Volts	Energy Calories per gm.-mol.	Wave-Length	Wave Number (cm^{-1})	Separation in band of 6000Å
Electronic	1–10	23 to 230 kgm.-cals.	12,350 to 1,235Å	8,100 to 81,000	(6000Å)
Oscillational or Vibrational	1/10	2.3 kgm.-cals. 2300 cals.	123,500Å =12.35μ	810	300Å
Rotational	1/1000	23 cals.	1235μ =0.1235 cm	8.1	3Å

Energy of 1 volt or 1 electron-volt = 1.591×10^{-12} erg 23.07 kgm.-cal. per gm.-mol.
1 calorie = 4.19×10^{7} ergs.

Hence the wave-length of the radiation caused by the emission of a single vibrational quantum of 0.1 volt energy is 123,500Å, or 12.35μ; that due to a rotational quantum of 0.001 volt energy is 1235μ or 0.1235 cm. On an electronic line of 6000Å (yellow light), the addition of one such vibrational quantum will make a difference of about 300Å, and that of a rotational quantum, of about 3Å. Spectroscopists commonly express their results, especially with band spectra and Raman spectra, in terms of wave-numbers (cm^{-1}) which are proportional to the frequencies but are referred to the centimeter and not to the second:

$$\text{wave-number} = \frac{\text{waves per second}}{\text{velocity of light}}$$

Table XIII gives the values of some of the relevant conversion factors.

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[16] See W. E. Garner and J. E. Lennard-Jones, *Trans. Faraday Soc.*, 25, 611 (1929).

[17] All values of dimensions given in this chapter are expressed in Ångströms (1Å 10^{-8} cm).

subdivided into a group separated only by something like 3Å. To a first approximation these rotational energy levels have an energy given by the expression

$$E_r = \frac{h^2K(K+1)}{8\pi^2 I}$$

where K is the rotational quantum number, and I is the moment of inertia of the molecule. It is this last fact which gives the band spectra their importance for our present purpose; they enable us to determine the moment of inertia of the molecule, which for a diatomic molecule is

$$I = \frac{m_1 . m_2}{m_1 + m_2} \times d^2$$

where m_1 and m_2 are the masses of the atoms, and d is the distance between them. Thus, as we know the masses we can calculate the distance.[18]

It should be observed that strictly speaking this distance is not quite the same as that given by the X-ray measurements. The moment of inertia is determined solely by the masses and hence by the nuclei of the atoms, and so gives us the internuclear distance. The X-ray scattering is not caused by the nuclei, but by the surrounding electrons; the "center" of the atom which it indicates is therefore not the nucleus, but the center of action of these electrons. For an isolated atom the two coincide; but the linked atoms are to some extent polarized, and hence a correction should be applied to the X-ray results.[19] With the crystal data this correction is usually negligible, because the deformation of the electronic orbits has much less effect when it is symmetrical,[20] but in the experiments with gases it may become measurable.

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[18] Since a gram-atom contains 6.062×10^{23} atoms, an atom of atomic weight A weighs $A \times 1.650 \times 10^{-24}$ gram. Hence for a molecule of two atoms with atomic weights A_1 and A_2:

$$I = \frac{A_1 . A_2}{A_1 + A_2} \times 1.650 \times 10^{-24} \times d^2$$

or

$$d^2 = 0.6062 \times 10^{24} \times I \times \frac{A_1 + A_2}{A_1 . A_2}$$

[19] See Debye, *Physik. Z.*, 31, 419 (1930); *Z. Elektrochem.*, 36, 612 (1930).

[20] It should however be taken into account in dealing with the less symmetrical crystals (Goldschmidt's "contrapolarization").

The magnitude of the rotational quanta, and hence the moments of inertia, may be determined in another way. These small amounts of energy can be emitted and absorbed by the molecule without any electronic jump, either alone or in association with vibrational quanta. Both kinds are so small (see Table XIII) that the resulting waves lie in the infra-red, the vibrational being about 10μ and the rotational about 1000μ, the latter appearing as a band structure of the former with a separation of the order of 0.01μ or 100Å. They can thus be observed by the methods of infra-red spectroscopy. The manipulation is difficult, however, and the measurements are far less accurate than those of visible or ultra-violet bands, since infra-red radiation cannot be photographed; but a considerable amount of work is being done in this direction.

A new method of observing infra-red frequencies was discovered by Raman in 1928.[21] He showed that if a strong beam of monochromatic light passes through a medium, the scattered light gives on resolution, in addition to the unchanged radiation, a series of lines lying on both sides of it. The differences of energy corresponding to the separation of these lines from that of the incident beam, agree with the energies of the infra-red spectrum of the medium where this is known. There can be no doubt that some of the incident light in the course of its reflection by the molecules of the medium loses or,—less frequently—picks up one or more quanta of the infra-red frequencies, oscillational or rotational. It is thus possible, by measuring the separation of the lines in such a spectrum, to find the wave-lengths of these infra-red lines.

This method has the great practical advantage that it brings the infra-red spectrum, so to speak, onto the photographic plate. It avoids the necessity of a rocksalt prism and the other parts of an infra-red spectrometer, and requires only the usual apparatus for visible and ultra-violet rays; and it substitutes the direct measurement of lines on a photographic plate for the troublesome and less accurate linear thermoelement. This phenomenon had been predicted by Smekal in 1923.[22] Since its experimental confirmation by Raman, it has been the subject of a very large number of investigations.[23] The experimental technique, which is difficult on account of the faintness of the scattered lines, has been developed largely through the work of Wood.[24]

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[21] C. V. Raman and K. S. Krishnan, *Nature*, 121, 501, 619 (1928); *Indian J. Phys.*, 2, 399 (1928).

These various methods of observing the absorption spectra are closely interrelated, and are complementary to one another; the interpretation of the results is often greatly assisted by combining two or more of them. In particular there are certain types of lines that appear in the absorption spectra and not in the Raman spectra, and others that are found only in the latter. By measurements in the far infra-red, at about 20–200μ, the rotational quanta can be observed directly. The experimental difficulties are peculiarly great here, however, partly from the lack of materials for the cells and prisms of the apparatus which do not themselves absorb in this region, and partly because the lines to be observed cover a range of so many octaves that it is difficult to distinguish between the different orders of spectra given by the gratings. In the near infra-red, at about 10μ, these difficulties are less. Here we observe the vibrational lines, with the rotational as a fine structure or as band spectra. In the visible and the ultra-violet regions the vibrational quanta appear as lines in a band, and the rotational as a fine structure of these lines. This part of the spectrum has the advantage that the technique is most highly developed; lenses and prisms of glass and quartz can be used, and the spectrum can be photographed; but the difficulties of correct assignment of the lines, with the possibility of overlapping bands, are considerable, and the rotational separations—especially with heavy molecules—are so small that a high resolving power is required. The Raman spectra have the advantage of greater simplicity, and are of especial value in the correct assignment of the vibrational levels.

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[22] A. Smekal, *Naturwissenschaften*, 11, 873 (1923).

[23] For a full discussion of the theory, and of the experimental data so far obtained, see K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Springer, Berlin 1931); also C. Schaefer and F. Matossi, *Fortschritte Chem., Physik, physik. Chem.*, 20, Heft 6 (1930). A more or less popular account of the use of the Raman spectrum as an instrument of research is given by D. H. Andrews, *J. Ind. Eng. Chem.*, 23, 1232 (1931).

[24] R. W. Wood, *Phys. Rev.*, 36, 1421 (1930); *Trans. Faraday Soc.*, 25, 792 (1929). See also N. N. Pal and P. N. Sen Gupta, *Indian J. Phys.*, 5, 609 (1930).

These investigations of the spectra tell us more than the distances between the atoms. In the first place they give us information about the shape of the molecule. It is theoretically possible, from a knowledge of all the moments of inertia of a molecule of, say, 3 or 4 atoms, to calculate all the interatomic distances and the valence angles. In particular, if the molecule is rectilinear, as with carbon dioxide or acetylene, this can be detected with certainty and the distances are then relatively easy to calculate. If it is triangular, like water or sulphur dioxide, this also can be detected; but the calculation of the distances and angles then becomes much more complicated, and it must be admitted that the attempts to determine these magnitudes have not, so far, been uniformly successful. Not only is there often disagreement between different investigators, but the distances that are calculated from the spectra often differ greatly from those derived from the effective radii. This, however, is a difficulty that will disappear, no doubt, as the subject is more developed, and the assignment of the various moments becomes more accurate.

One further complication must be mentioned. The internuclear distances that we desire to know are those which occur in the normal resting state of the molecule. The spectroscopic methods, except the direct measurements of the rotational lines in the far infra-red, always deal with molecules excited electronically or vibrationally, or in both ways. These excitations will have an effect on the distances. Sometimes it is uncertain whether the electronic state to which the vibrational and rotational quanta refer is really the "ground state" of the molecule, that is, whether the distance we are measuring is that which the link normally has or that which it has when the molecule is excited.

The vibrational quanta further tell us the magnitude of the force that resists a change in the interatomic distance. This force is of great interest, but as it concerns the strength of the link it is discussed in the next chapter.

Measurement with Cathode Rays

As has already been mentioned, a new method for measuring interatomic distances, especially in gases and vapors, has been developed by Wierl,[25] which resembles Debye's method of the scattering of X-rays, except that it substitutes cathode rays (electrons) for the X-rays. Electrons in motion are accompanied by, or consist of, or behave as if they consisted of waves whose length, λ, is given by $\lambda = h/mv$, where m is the mass and v the velocity of the electron.[26] When a narrow pencil of electrons passes through a vapor, the electrons are scattered, and the interference patterns produced by their waves can be recorded on a photographic plate. Thus the general nature of the process is the same as in Debye's experiments with X-rays. The electron method has however two advantages: the interaction between the electrons and the molecules of the gas is much more intense than it is with X-rays, and the electrons have a stronger photographic effect. These two causes cut down the time of exposure to not more than 1/10,000 of that required for X-rays. In Wierl's experiments electrons of about 40 kilowatts energy (wavelength 0.06Å) were used, and the exposures required were not more than a few tenths of a second. This is more than a mere practical convenience; it greatly extends the range of substances to which the method can be applied. In the X-ray experiments exposures of several hours are necessary, even when the chamber is filled with vapor under atmospheric pressure; if the pressure were much reduced the exposures would become impossibly long. But there are many substances that decompose at temperatures below those at which they boil under atmospheric pressure, while they boil without decomposition under reduced pressure. Such substances can readily be examined by the electron method with its much shorter exposures.

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[25] H. Mark and R. Wierl, *Z. Physik*, 60, 741 (1930); *Z. Electrochem.*, 36, 675 (1930); *Naturwissenschaften*, **18**, 205 (1930); R. Wierl, *Physik. Z.*, **31**, 366, 1028 (1930); "Elektroneninterferenzen" in *Leipziger Vorträge* (Leipzig, 1930) page 13; *Ann. Physik*, 8-[v], 521 (1931); H. Gazewski, *Physik. Z.*, **32**, 219 (1921).

[26] This is the relation of L. de Broglie. For its experimental verification see C. Davisson and L. H. Germer, *Phys. Rev.*, 30, 707 (1927); G. P. Thomson, *Nature*, **122**, 279 (1928), and *Wave Mechanics of Free Electrons* (New York, 1930), p. 47 (George Fisher Baker Nonresident Lectureship at Cornell, Vol. 8).

Where they are applied to the same substances the two methods give concordant results. Wierl claims for his measurements an accuracy rather greater than that of the X-ray method; but a careful discussion by Bewilogua of the errors of the two methods seems to show that the latter is rather more accurate.[27]

A list of the results so far obtained by these new methods is given in Table XXI (page 89). In view of Bewilogua's conclusions the probable error is quoted only for the X-ray values.

RESULTS OF MEASUREMENTS

The results are divisible into three classes according to the nature of the material and the kind of links which it contains: (1) salts, (2) metals, (3) covalent compounds. These last can be examined both in the solid and in the gaseous state. It does not seem, however, that the state of aggregation makes much difference in the distance between the atoms in a covalent link; and this is to be expected, since the forces between the molecules of a solid covalent compound are small in comparison with those between the component atoms of the molecule.[28] The crystalline data are by far the most numerous; their collection and co-ordination is largely the work of V. M. Goldschmidt and his pupils.[29]

While we are mainly concerned with the values for the covalent link, it is necessary to consider those for the ions as well, since the size of the link is often of assistance in deciding to which of the two classes a compound should be assigned. Thus the first question which arises is the influence of ionization on the atomic radius. This is certainly large, and it would therefore seem that it should be easy to determine, by measuring its length, whether a link in a molecule is ionized or not. But the effects of a negative and a positive charge are in the opposite directions, the former increasing and the latter diminishing the radius; they therefore neutralize one another in a salt to a considerable extent, and while the radius of each atom is very different according as it is ionized or covalent, the effect of the nature of the link on the sum of the two radii, which is what we measure, is much less. In fact it is of much the same order as the differences caused by other influences, especially by the type of crystal lattice. Goldschmidt emphasizes the importance of the distance as a criterion of the nature of the link but, though he is certainly justified in doing so, the test needs care and is not so obvious as one would imagine from the large difference in the two states of either atom taken alone. In any series of similar compounds the change from one form of linkage to the other can be detected by the dimensions, as it can in many groups by the change of lattice, but it is sometimes difficult to say to which type an isolated series of compounds should be assigned.

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[27] Bewilogua, *Physik. Z.*, 32, 114 (1931).

[28] In carbon tetrachloride, for example, as we have seen, the latent heats of fusion and of evaporation are both about 7 kgm.-cal. per gm.-mol., while the separation of the CCl_4 molecules into their component atoms needs about 270 kgm.-cal.

[29] V. M. Goldschmidt, "Geochemische Verteilungsgesetze," VII (Oslo, 1926); *idem*, VIII (Oslo, 1927). A list of values based upon the X-ray data is given by Goldschmidt in *Ber.*, 60, 1263 (1927); another agreeing with this in the main, but based upon quantum mechanics, is given by Pauling in *J. Am. Chem. Soc.*, 49, 765 (1927). The data for the solid elements have been collected by Neuburger in *Z. Krist.*, 80, 103 (1931) and published separately as *Gitterkonstanten 1931* (Leipzig, Akademisches Verlagsges.). A revised list of the ionic radii of ions with the inert gas structure is given by Zachariasen in *Z. Krist.*, 80, 137 (1931). The theory contained in this paper is referred to later. An interesting discussion of the subject, particularly in its bearing on carbon and carbon compounds, is to be found in K. H. Meyer and H. Mark, *Aufbau der hochpolymeren organischen Naturstoffe* (Leipzig, 1930), Chapters I and II.

The values obtained from the measurements of salts are, of course, always the sum of the radii of two ions of opposite character. In order to get values for individual ions we must determine by other means the radii of one or two particular ions. Goldschmidt takes the radius of the fluorine ion F^- as 1.33Å, and that of the oxygen ion O^{--} as 1.32Å. These values are the basis on which all his other ionic radii are calculated. The concordance among the values for the ions obtained from the crystal measurements by their use is really no evidence for their truth. Any other values which made the fluorine ion 0.01Å larger than the oxygen ion would be equally satisfactory from this point of view. They are however quite well established, with a probable error not exceeding 0.01Å, by the agreement of the following five different lines of argument:

(1) Wasastjerna[30] has calculated the values from the molecular refraction on the basis of the Clausius-Mosotti law.

(2) Goldschmidt has shown that the change which occurs in many series of salts, from one type of lattice to another, is determined by the relative sizes of the ions, and takes place when the new lattice involves a closer packing than the old. This gives us an independent check on the relative sizes of the oppositely charged ions.

(3) The calculations of Pauling and Hartree, based on wave mechanics, lead to the same values.

(4) The values of the diamagnetic susceptibilities of the ions also agree.

(5) The curves obtained by Bragg for the intensities of the X-ray reflections give further confirmation.

We may therefore accept Goldschmidt's values as correct for these two ions,[31] and the radii of all the other ions can be obtained from them.

The differences produced by ionization are indicated by the examples given in Table XIV, in which the values for the ions are taken from measurements with salts, and those for the neutral atoms are from the metals or from covalent compounds.

TABLE XIV

Atomic Radii

		K	Ca	Zn
Radius of	neutral atom X	2.31	1.97	1.32
	cation X^+, X^{++}	1.33	1.06	0.83

		H	Br	O	Se
Radius of	neutral atom X	0.37	1.13	0.60	1.16
	anion X^-, X^{--}	1.36	1.96	1.32	1.91

	Fe atom	Fe^{++}	Fe^{+++}	Tl atom	Tl^+	Tl^{+++}
Radius	1.27	0.83	0.67	1.71	1.49	1.05

The expected effect of the positive charge in diminishing, and that of the negative charge in increasing, the radius is obvious.

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[30] J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys-Math.*, 1 (1923), Art. 38, p. 22; *Z. physik. Chem.*, 101, 193 (1922); K. Fajans and G. Joos, *Z. Physik*, 23, 1 (1924).

[31] Zachariasen, *Z. Krist.*, 80, 137 (1931), also comes to this conclusion for the fluorine ion. His value for O^{--} is not directly comparable with Goldschmidt's.

The values so obtained represent only approximately the radii in actual crystals. As we have already seen (p. 30) the distances are not strictly additive, even in salts of the same type. We may distinguish three kinds of influences which affect the values, though all of them to only a small extent. There is first the temperature and pressure under which the measurements are made; for exact comparison the values should be those at zero pressure and zero temperature.[32] The effect of pressures not exceeding a few atmospheres may however be neglected. The temperature correction can be made from the coefficients of expansion if it is necessary, but it will seldom affect the values more than one or two per cent. A more serious effect is that due to the deformation of the ions, already considered in Chapter II. To show the magnitude of this effect, the values for the alkaline halides are given in Table XV (below), along with those calculated by Goldschmidt's method, which is arranged to fit the potassium

TABLE XV

Interatomic Distances in Alkaline Halides

	LiF	NaF	KF	RbF	CsF
Calc.	2.11		2.66	2.82	2.98
Obs.	2.04		2.66	2.82	3.00
Diff.	−0.07	±0.0	±0.0	±0.0	+0.02
	LiCl	NaCl	KCl	RbCl	[CsCl]
Calc.	2.59	2.79	3.14	3.30	3.46
Obs.	2.57	2.81	3.14	3.29	3.56
Diff.	−0.02	+0.02	±0.0	−0.01	[+0.06]
	LiBr	NaBr	KBr	RbBr	[CsBr]
Calc.	2.74	2.94	3.29	3.45	3.61
Obs.	2.75	2.98	3.29	3.43	3.71
Diff.	+0.01	+0.04	±0.0	−0.02	[+0.11]
	LiI	NaI	KI	RbI	[CsI]
Calc.	2.98	3.18	3.53	3.69	3.85
Obs.	3.03	3.23	3.53	3.66	3.95
Diff.	+0.05	+0.05	±0.0	−0.03	[+0.10]

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[32] For an alternative method of eliminating the temperature effect see below, p. 90.

salts. All these salts are of the sodium-chloride (6:1) lattice, except the three cesium salts enclosed in brackets, which have the cesium-chloride (8:1) lattice. It will be seen that so long as the lattice remains the same, the differences do not exceed 2 or 3 per cent, and are normally much less.

Another influence (indicated in Table XV) is the nature of the lattice. Goldschmidt has shown that the distances suffer a small but quite definite change with a change of what he calls the "co-ordination number." This number has nothing to do with co-ordination in its usual chemical sense; it is merely a name for the number of nearest neighbors[33] by which each atom in the lattice is surrounded. In the sodium-chloride lattice, for example, each ion is surrounded by 6 of the opposite kind; in the cesium-chloride lattice the number is eight. Goldschmidt finds that a fall in the "co-ordination number" leads to a decrease in the interatomic distances as shown in Table XVI.

TABLE XVI

Change in Atomic Distance with change in "Co-ordination Number"

"Co-ordination Number" change from		Decrease in distance Per cent
6 to 4		5–7
8 to 6		3
12 to 8		3
12 to 8	in metals	2.8–3.5
12 to 6		4
12 to 4		11–12

These changes occur in metals as well as in salts, and possibly, though this is less certain, in non-ionized compounds as well.

This question of deformation has recently been discussed in detail by Zachariasen.[34] He works out the corrections to be applied for (1) the co-ordination number, and (2) the valency. He gives a series of values for the radii of the ions, and shows by a large number of examples that when they are corrected by his method, they give a remarkably close agreement with the observed values in salts. The paper is of great interest, but cannot be discussed further here, as we are concerned with covalent links. Zachariasen has not considered covalent compounds in detail, but he finds that his conclusions for salts will not apply to them without at least considerable modification, as we should expect.

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[33] "Wir betrachten also nur die nächsten Nachbarn eines Krystallbausteines."—Goldschmidt, "Geochemische Verteilungsgesetze . . .," VIII, 23 (1927).

[34] W. H. Zachariasen, *Z. Krist.*, 80, 137 (1931).

When allowance is made for these modifying influences, it can be shown that there is a definite change in the distance when the link passes from electrovalent to covalent. The two classes of compounds are, as Goldschmidt calls them, "incommensurable"; the values of the radii which express the distances in one class cannot be used for the other. The most striking example is given by the two forms of silver iodide, where the distance in the ionic α-form is 3.05Å and in the covalent β-form 2.81Å, a difference of nearly 9 per cent. The sum of the atomic radii in metallic silver and gaseous chlorine is almost exactly equal to the latter value, being 2.77Å. Another example is given by the differences between the distances in the sulphides and oxides of the metals beryllium, zinc, and cadmium. All these compounds are covalent except cadmium oxide, where the link, being electrovalent, is longer,[35] and hence the difference from the sulphide smaller:

Metal, X	Be	Zn	Cd
(X—S)−(X—O)	0.45	0.38	0.17

The occurrence of one or the other kind of link is closely connected also with the type of lattice, although some types occur with both forms of link. According to Goldschmidt the two incommensurable classes of links are found respectively in the following lattices; the figures in brackets, as [8], indicate the "co-ordination number" in the sense defined above.

A. Covalent Lattices

(1) Zinc blend, [4]
(2) Wurtzite, [4]
(3) Cuprite, AX_2, [4,2]
(4) Diamond, [4]

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[35] See page 50.

These four types of lattice are strictly commensurable (within 1 per cent), and seem never to occur with ionic structures, probably because they are so far removed from close packing.

(5) Regular body-centered, [8], distances up to 3 per cent smaller than in (6).
(6) Regular face-centered, [12].
(7) Closest hexagonal packing, [12].

These last three types are especially frequent in metals. They are certainly commensurable among themselves, and probably also with the first four.

(8) The hexagonal nickel-arsenide type, [6].

This is an entirely different lattice from the sodium-chloride type. Every cation (A) has six anions (X) almost at the angles of a regular octahedron; every X has six A's at the angular points of a trigonal prism with X as center. This lattice may also belong to this group, or it may possibly form a separate commensurable group with other arsenides and sulphides.

To these must be added certain individuals of types usually belonging to Class B (ionic lattices); some of the sodium-chloride and fluorite types, such as the mononitrides of titanium and zirconium; the cubic Cu_2S; and probably TlSb and TlBi, with cesium-chloride structure.

B. Ionic Lattices

(1) NaCl type, [6].
(2) CsCl type, [8]
(3) Fluorite, AX_2, [8,4].
(4) Rutile, AX_2, [6,3].
(5) Probably the perowskite type in certain compounds, but some of this type and many of the rutile type are covalent.[36]

These show the small differences in magnitude referred to above; cesium-chloride lattices give values always about 3 per cent, and rutile lattices often as much as 5 per cent greater than the sodium-chloride; the values for sodium-chloride and fluorite lattices are almost identical.

The evidence for the view that crystals of Class A have covalent, and those of Class B electrovalent links, is of very various kinds. The values of the radii given by Class A are those that hold for the covalent molecules of the volatile elements; the alkaline halides, which are undoubtedly ionized in the solid as well as in the dissolved and gaseous states (see p. 57), belong to Class B. It is only compounds of Class A that dissolve in metals (*e.g.* cuprous oxide, Cu_2O, in copper, ferrous sulphide in iron). The change from Class B to Class A, among compounds of similar composition, always occurs when on the Fajans theory an increase in deformation is to be expected. The wider spacing (less close packing) of the atoms in most of the lattices in Class B is a sign of the directive character of covalent as compared with electrovalent links. The distinction is now so well established that the crystal lattices can be used with reasonable certainty to determine whether a compound is ionized in the solid state or not.

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[36] Goldschmidt regarded the rutile lattice as normally ionic; but many of his measurements agree better with values for a covalent lattice.

When we examine the data for molecules with covalent links it becomes obvious that the interatomic distance is remarkably constant, and very little affected by the conditions of the molecule or by the other links that it contains. This is illustrated by the values obtained for the link of carbon to carbon, with different substances and by different methods, which are collected in Table XVII below.

TABLE XVII

Interatomic Distances, in Ångström Units

Link	Substance	Distance	Method
C—C	Diamond	1.54	Crystal structure
	Solid ethane	1.6	Crystal structure
	n-Paraffins	1.58	Crystal structure
	Side chain $C_6(CH_3)_6$	1.55	Crystal structure
	Cyclohexane	1.51	Electron scattering
	Pentane	1.5	Electron scattering
C—C aromatic	Graphite	1.42	Crystal structure
	$C_6(CH_3)_6$	1.45	Crystal structure
	Naphthalene Anthracene	1.45	Crystal structure
	Benzene	1.4 1.39	X-ray scattering Electron scattering
C═C	Stilbene	1.31	Crystal structure
	Swan Bands	1.35	Spectrum
C≡C	Acetylene	1.19	Spectrum

In the same way the distance $N\equiv N$ in solid nitrogen is 1.10Å, and in nitrogen gas, from the band spectrum, is 1.107Å. The same constancy is found when we compare the observed distances in covalent compounds with the sum of the effective radii (half the interatomic distances) found for the elements themselves. One modifying influence which has to be taken into account here is that of the multiplicity of the link. As Table XVII shows, the double link of carbon to carbon is markedly shorter than the single link, and the triple link is shorter still. We have no data as to the effect in other elements, but we may fairly assume that it is of the same order, and as a first approximation that the same percentage contraction occurs. This conclusion is supported by the fact that the interatomic distances in the successive elements carbon, nitrogen, oxygen, fluorine, form a much more regular series if they are corrected for the multiplicity of the link in this way. In carbon we have $C-C$ 1.54; $C=C$ 1.32; $C\equiv C$ 1.19; the double link is 14 per cent and the triple is 23 per cent shorter than the single. Applying the same percentage corrections to nitrogen and to oxygen we get:

	$C-C$	$N\equiv N$	$O=O$	$F-F$
Observed	1.54	1.10	1.20	1.35
Correction:	—	0.32	0.20	—
	$C-C$	$N-N$	$O-O$	$F-F$
Corrected value:	1.54	1.42	1.40	1.35

In the same way we get for double and triple links:

$C=C$	$N=N$	$O=O$
1.32	1.22	1.20
$C\equiv C$	$N\equiv N$	$O\equiv O$
1.19	1.10	1.08

That this method of correction is near the truth is shown by the observations of the link of carbon to nitrogen which in hexamethylene tetramine, where it is single, is found to be 1.48, and in cyanogen, where it is triple, to be 1.15Å. The corrected calculated values are identical with the observed.

The values of the effective radii, obtained by halving the distance between the atoms in the elements themselves, are given in Table XVIII. The data for the solid elements are from Neuburger's *Gitterkonstanten 1931*,[29] those for the ions are from Zachariasen[37] and Goldschmidt.[38] These latter include some ions to which there is no reason to ascribe any real existence, such as C^{4+}, the molecules that are supposed to contain them being obviously covalent.

Table XIX contains a series of observed values of the dimensions of links in compounds, which are compared with the sums of the radii taken from Table XVIII. With these, corrections for double and triple links are either unnecessary, or are impossible for want of knowledge of the state of linkage in the elements, largely metals, from which the atomic radii are derived. Table XX contains a series of links, mostly organic, for which the calculated values can be corrected in this way.

As will be seen, the agreement between the calculated and observed values for the covalent links is almost invariably very close. In Table XIX a few ionized compounds

TABLE XVIII

Effective Radii of Neutral Atoms and Ions

(In Ångström Units)

Element	Atom			Ion	
H	0.37	gas	H^-	1.36^{z}	1.27^{G}
He	0.53				
Ne	1.60	crystal			
A	1.91	crystal			
Kr	1.98	crystal			
X	2.18	crystal			
Li	1.50^{N}	1.51^{HR}	Li^+	0.68^{z}	0.78^{G}
Na	1.84^{N}	1.84^{HR}	Na^+	0.98^{z}	0.98^{G}
K	2.31^{N}	2.27^{HR}	K^+	1.33^{z}	1.33^{G}
Rb	2.44^{N}	2.43^{HR}	Rb^+	1.48^{z}	1.49^{G}
Cs	2.62^{N}	61^{HR}	Cs^+	1.67^{z}	1.65^{G}
Cu	1.28^{N}	29^{HR}	Cu^+	—	ca. 1.0^{G}
Ag	1.44^{N}	42^{HR}	Ag^+	—	1.13^{G}
Au	1.44^{N}	45^{HR}	—	—	
Be	1.12^{N}	1.16^{HR}	Be^{2+}	0.39^{z}	0.34^{G}
Mg	1.60^{N}	1.58^{HR}	Mg^{2+}	0.71^{z}	0.78^{G}
Ca	1.97^{N}	1.98^{HR}	Ca^{2+}	0.98^{z}	1.06^{G}
Sr	2.15^{N}	2.11^{HR}	Sr^{2+}	1.15^{z}	1.27^{G}

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[37] Zachariasen, *Z. Krist.*, 80, 137 (1931).

[38] Goldschmidt, *Ber.*, 60, 1263 (1927).

TABLE XVIII (continued)

Effective Radii of Neutral Atoms and Ions

(In Ångström Units)

Element	Atom			Ion	
Ba	2.17^{N}	2.30^{HR}	Ba^{2+}	1.31^{Z}	1.43^{G}
Zn	1.32^{N}	—	Zn^{2+}	—	0.83^{G}
Cd	1.49^{N}	—	Cd^{2+}	—	1.03^{G}
Hg	1.50^{N}	—	Hg^{2+}	—	1.12^{G}
B	(ca. 0.7)	—	B^{3+}	0.24^{Z}	
Al	1.43^{N}	—	Al^{3+}	0.55^{Z}	0.57^{G}
Sc	—	—	Sc^{3+}	0.78^{Z}	0.57^{G}
Y	—	—	Y^{3+}	0.93^{Z}	1.06^{G}
La	1.86^{N}	—	La^{3+}	1.06^{Z}	1.22^{G}
Ce	1.81^{N}	—	Ce^{3+}	—	1.18^{G}
			Ce^{4+}	0.92^{Z}	1.02^{G}
Pr	—	—	Pr^{3+}	—	1.16^{G}
			Pr^{4+}	—	1.00^{G}
Gd		—	Gd^{3+}	—	1.11^{G}
Er	1.86^{N}	—	Er^{3+}	—	1.04^{G}
Lu	—	—	Lu^{3+}	—	0.99^{G}
Ga	1.24^{N}	—	Ga^{3+}	—	0.62^{G}
In	1.62^{N}	—	In^{3+}	—	0.92^{G}
Tl	1.71^{N}	—	Tl^{+}	—	1.49^{G}
			Tl^{3+}	—	1.05^{G}
C—	0.771	0.78^{HR}	C^{4+}	0.19^{Z}	0.20^{G}
C═	0.67	Sp. cryst.		—	—
	0.60	Sp. C_2H_2		—	—
Si	1.17^{N}	1.16^{HR}		—	—
Ge	1.22^{N}	—	Ge^{4+}	—	0.44^{G}
Sn	1.51^{N}	(white)	Sn^{4+}	—	0.74^{G}
Pb	1.75^{N}		Pb^{2+}	—	1.32^{G}
			Pb^{4+}	—	0.84^{G}
Ti	1.45^{N}	1.49^{HR}	Ti^{4+}	0.62^{Z}	0.64^{G}
Zr	1.58^{N}	1.62^{HR}	Zr^{4+}	0.79^{Z}	0.87^{G}
Hf	1.57^{N}	1.65^{HR}			—
Th	1.79^{N}	1.83^{HR}	Th^{4+}		1.10^{G}
N—	0.71	calc.	N^{5+}	0.32^{Z}	—
			N^{3-}	2.02^{Z}	—
N═	0.61	calc.			—
N≡	0.55	gas, cryst.			—
P	0.87^{N}	(metal.)	P^{5+}	0.66^{Z}	—
			P^{3-}	2.56^{Z}	—
As	1.25^{N}	1.25^{HR}	As^{3-}	2.62^{Z}	—

TABLE XVIII (concluded)

Effective Radii of Neutral Atoms and Ions

(In Ångström Units)

Element	Atom			Ion	
Sb	1.45^{N}	1.45^{HR}	Sb^{3-}	2.77^{Z}	—
Bi	1.55^{N}	1.54^{HR}		—	—
V	1.30^{N}	—	V^{5+}	0.82^{Z}	—
			V^{4+}		0.61^{G}
Cb	1.43^{N}	—	Cb^{5+}	0.98	—
			Cb^{4+}	—	0.69^{G}
Ta	1.42^{N}	—		—	—
O—	0.70	calc.	O^{2-}	1.40^{Z}	1.32^{G}
O=	0.60	gas		—	—
S—	1.06	—	S^{2-}	1.85^{Z}	1.74^{G}
S=	0.92	calc.		—	—
Se	1.16^{N}	—	Se^{2-}	1.96^{Z}	1.91^{G}
			Se^{6+}	—	$0.3\text{–}0.4^{\mathrm{G}}$
Te	1.44^{N}	—	Te^{2-}	2.18^{Z}	2.11^{G}
			Te^{4+}	—	0.89^{G}
Cr	1.25^{N}	1.25^{HR}	Cr^{3+}	—	0.65^{G}
Mo	1.36^{N}	1.35^{HR}	Mo^{4+}	—	0.68^{G}
W	1.37^{N}	1.37^{HR}	W^{4+}	—	0.68^{G}
U	1.49^{N}	—	U^{4+}	—	1.05^{G}
F	0.68^{N}	—	F^{-}	1.33^{Z}	1.33^{G}
Cl	0.97^{N}	—	Cl^{-}	1.81^{Z}	1.81^{G}
Br	1.13^{N}	—	Br^{-}	1.96^{Z}	1.96^{G}
I	1.35^{N}	—	I^{-}	2.19^{Z}	2.20^{G}
Mn	1.18^{N}	—	Mn^{2+}	—	0.91^{G}
			Mn^{4+}	—	0.52^{G}
Re	1.37^{N}	—		—	
Fe	1.27^{N}	1.26^{HR}	Fe^{2+}	—	0.83^{G}
			Fe^{3+}	—	0.67^{G}
Co	1.25^{N}	1.26^{HR}	Co^{2+}	—	0.82^{G}
Ni	1.24^{N}	1.26^{HR}	Ni^{2+}	—	0.78^{G}
Ru	1.32^{N}	1.35^{HR}	Ru^{4+}	—	0.65^{G}
Rh	1.34^{N}	1.35^{HR}	Rh^{3+}	—	0.69^{G}
Pd	1.37^{N}	1.37^{H}		—	—
Os	1.34^{N}	1.[illegible]	Os^{4+}	—	0.67^{G}
Ir	1.35^{N}	1.35^{HR}	Ir^{4+}	—	0.66^{G}
Pt	1.38^{N}	1.39^{HR}		—	—

[G] V. M. Goldschmidt, *Ber.*, 60, 1263 (1927).
[HR] W. Hume-Rothery, *Phil. Mag.*, [7]10, 217 (1930), theoretical values.
[N] M. C. Neuburger, *Gitterkonstanten 1931* (Leipzig).
[Z] W. H. Zachariasen, *Z. Krist.*, 80, 137 (1931).

TABLE XIX

Interatomic Distances (In Ångström Units)

Link	Distance		Compound	Type	Ref.*
	Calc.	Obs.			
Li[F]	2.18	2.04	LiF	NaCl	12
Li[I]	2.85	3.03	LiI	NaCl	12
K[F]	2.99	2.66	KF	NaCl	12
K[I]	3.66	3.53	KI	NaCl	12
Cs[F]	3.30	3.00	CsF	NaCl	12
Cs[I]	3.97	3.95	CsI	CsCl	12
Cu—Cl	2.25	2.34	CuCl	Zinc blende	2
Cu—Br	2.41	2.46	CuBr	Zinc blende	2
Cu—I	2.63	2.62	CuI	Zinc blende	2
Cu—O	1.88	1.85	Cu_2O	—	3
Cu—S	2.34	2.31	Cu_2S	Fluorite	4
Cu—Se	2.44	2.49	Cu_2Se	Fluorite	4
Cu—Zn	2.60	2.60	CuZn	—	4
Cu—Pd	2.65	2.64	CuPd	—	4
Ag[F]	2.12	2.46	AgF	NaCl	3
Ag[Cl]	2.41	2.77	AgCl	NaCl	4
Ag[Br]	2.57	2.88	AgBr	NaCl	4
Ag[I]	2.79	3.05	AgI α	NaCl	4
Ag—I	2.79	2.81	AgI β	Zinc blende	4
Ag—O	2.04	2.04	Ag_2O	Cuprite	4
Be—O	1.72	1.65	BeO	Wurtzite	2
Be—S	2.18	2.10	BeS	Zinc blende	4
Be—Se	2.28	2.18	BeSe	Zinc blende	12
Mg[F]	2.28	1.99	MgF_2	Rutile	4
Mg[O]	2.20	2.10	MgO	NaCl	4
Ca[F]	2.65	2.36	CaF_2	Fluorite	4
Zn—F	2.00	2.04	CaF_2	Rutile	4
Zn—O	1.92	1.97	ZnO	Wurtzite	4
Zn—S	2.38	2.35	ZnS	Wurtzite	4
Zn—Se	2.48	2.45	ZnSe	Zinc blende	2
Cd[O]	2.09	2.35	CdO	NaCl	4
Cd—S	2.55	2.53	CdS	Wurtzite	4
Cd—Se	2.65	2.63	CdSe	Wurtzite	4
Cd—Te	2.93	2.80	CdTe	Zinc blende	4
Hg—I	2.85	2.75	HgI_2	—	13
Hg—S	2.56	2.53	HgS	Zinc blende	4
Hg—Se	2.66	2.63	HgSe	Zinc blende	4
Al—N	1.98	1.87	AlN	Wurtzite	2
Al—P	2.30	2.36	AlP	Zinc blende	2
Ga—As	2.49	2.44	GaAs	Zinc blende	4
Ga—Sb	2.69	2.64	GaSb	Zinc blende	4
Tl[Cl]	2.68	3.32	TlCl	CsCl	3
Tl[I]	3.06	3.62	TlI	CsCl	4

* Refer to list on page 88.

TABLE XIX (concluded)

Link	Distance Calc.	Distance Obs.	Compound	Type	Ref.*
Sn—Cl	2.48	2.45	K_2SnCl_6		1
Sn—O	2.11	2.06	SnO_2	Rutile	3
Sn—S	2.57	2.55	SnS_2	CdI_2	4
Pb—I	3.10	3.18	PbI_2	CdI_2	4
Pb—O	2.35	2 33	PbO	—	3
Ti—O	2.05	1 96	TiO_2	Rutile	3
Ti—S	2.51	2.42	TiS_2	CdI_2	4
Ti—Se	2.61	2.54	$TiSe_2$	CdI_2	4
Ti—C	2.22	2.30	TiC	—	3
Zr—O	2.18	2.21	ZrO_2	Fluorite	4
Zr—S	2.64	2.58	ZrS_2	CdI_2	4
Zr—Se	2.74	2.68	$ZrSe_2$	CdI_2	4
Zr—C	2.35	2.37	ZrC	—	3
As—Ni	2.49	2.42	NiAs	NiAs	3
Sb—Cr	2.70	74	CrSb	NiAs	3
Sb—Fe	2.72	67	Fe_xSb_y	NiAs	4
V—O	1.90	93	VO_2	Rutile	3
V—C	2.07	15	VC	—	3
Cb—O	2.03	2.01	CbO_2	Rutile	3
Cb—O	2.03	2.01	$KCbO_3$	—	3
Cb—C	2.20	2.20	CbC	—	3
Ta—C	2.19	2.21	TaC	NaCl	4
S—O	.66	1.66	M_2SO_4	—	3
Mo—O	.96	2.00	MoO_2	Rutile	4
Mo—O	.96	2.00	Ag_2MoO_4	—	1
W—O	.97	2.00	WO_2	Rutile	4
F—H	.05	0.92	HF	Band spectrum	9
Cl—H	.34	1.27	HCl	Band spectrum	9
Br—H	.50	1.41	HBr	Band spectrum	9
I—H	1.72	1.61	HI	Band spectrum	9
I—Cl	2.32	2.26	$CsICl_2$	—	1
Co[O]	1.85	2.13	CoO	NaCl	4
Co—S	2.31	2.33	CoS	NiAs	4
Co—Se	2.41	2.45	CoSe	NiAs	4
Co—Te	2.69	2.62	CoTe	NiAs	4
Ni—S	2.30	2.38	NiS	NiAs	4
Ni—Se	2.40	2.50	NiSe	NiAs	4
Ni—Te	2.69	2.65	NiTe	NiAs	4
Ru—O	1.92	1.97	RuO_2	Rutile	3
Rh—O	1.94	2.01	Rh_2O_3	Corundum	3
Pd—Cl	2.34	2.29	K_2PdCl_4	—	1
Os—O	1.94	1.99	OsO_2	Rutile	3
Ir—O	1.95	1.98	IrO_2	Rutile	3
Pt—Cl	2.35	2.29	K_2PtCl_6	—	8
Pt—Cl	2.35	2.27	K_2PtCl_4	—	1

* Refer to list on page

are included which are distinguished by having brackets about the second element, as Ag[Cl]. They show the characteristic "incommensurability" to which Goldschmidt has drawn attention.

The close agreement between calculation and observation is remarkable in those links where one of the radii

TABLE XX

Interatomic Distances, Calculated distances being corrected for Multiple Links

(In Ångström Units)

Link	Distance		Compound	Method	Ref.*
	Calc.	Obs.			
C—H	1.14	1.12	Saturated hydrocarbons	Band spectrum	
C—H	1.14	.08	C_2H_2	Band spectrum	11
C—N	1.48	.48	Hexamethylene tetramine	Crystal	
C≡N	1.15	.15	C_2N_2	Band spectrum	9
C═O	1.26	.15	CO_2	Band spectrum	14
C≡O	1.14	.14	CO	Band spectrum	15
C—Cl	1.74	1.83	CCl_4 vap.	X-ray	16
				Electron ray	17
N—H	1.08	0.98	NH_3	Band spectrum	7
O—Cl	1.67	1.56	$MClO_4$	Crystal	10

*References to Tables XIX and XX:

[1] R. W. G. Wyckoff, *The Structure of Crystals* (Am. Chem. Soc. Monogr., 19, 1924), pp. 400-402.

[2] V. M. Goldschmidt, *Z. Elektrochem.*, 34, 459 (1928).

[3] ————, *Geochemische Verteilungsgesetze der Elemente*, VII. (Oslo, 1926).

[4] ————, *ibidem*, VIII. (Oslo, 1927).

[5] A. Müller, *Proc. Roy. Soc. London*, 114, 542 (1927); *ibidem*, 120, 437 (1928).

[6] H. W. Correll and H. Mark, *Z. physik. Chem.*, 107, 181 (1923).

[7] R. M. Badger and R. Mecke, *Z. physik. Chem.*, B5, 333 (1929).

[8] Frederikse and Verweel, *Rec. trav. chim.*, 47, 904 (1928).

[9] R. Mecke, *Bandspeksra* (Berlin, 1929), pp. 22-29.

[10] W. H. Zachariasen, *Z. Krist.*, 73, 141 (1930).

[11] K. Hedfield and R. Mecke, *Z. Physik*, 64, 151 (1930); W. H. J. Childs and R. Mecke, *Z. Physik*, 64, 162 (1930); R. Mecke, *Z. Physik*, 64, 173 (1930); *Z. Elektrochem.*, 36, 803 (1930).

[12] W. H. Zachariasen, *Z. Krist.*, 80, 137 (1931).

[13] Ketelaar, *Z. Krist.*, 80, 190 (1931).

[14] W. H. Keesom and J. de Smedt, *Proc. Acad. Sci. Amsterdam*, 27, 839 (1924); H. Mark and E. Pohland, *Z. Krist.*, 61, 293 (1925); *ibid.*, 64, 113 (1926); H. Kruner, *Z. Krist.*, 63, 275 (1926).

[15] C. Schaefer and F. Matossi, *Das ultrarote Spektrum* (Berlin, 1930).

[16] P. Debye, *Z. Elektrochem.*, 36, 612 (1930).

[17] L. Bewilogua, *Physik. Z.*, 32, 265 (1931).

TABLE XXI

Interatomic Distances in Vapor

Substance	Gap	X-ray		Cathode ray		Remarks
		Å	Ref.	Å	Ref.	
CCl_4	Cl—Cl	2.99+0.03	2	2.98	3	
$CHCl_3$	Cl—Cl	3.11+0.05	2	3.04	3	
CH_2Cl_2	Cl—Cl	3.23 ±0.1	2	3.16	3	
CH_3Cl	C—Cl	1.9 +0.1	2	1.85	3	
$SiCl_4$	Cl—Cl	—		3.29	5	tetrahedral
$GeCl_4$	Cl—Cl	—		3.43	5	tetrahedral
$TiCl_4$	Cl—Cl	—		3.61	5	tetrahedral
$SnCl_4$	Cl—Cl	—		3.81	5	tetrahedral
CBr_4	Br—Br	—		3.35	5	tetrahedral
BCl_3	Cl—Cl	—		3.03	5	?
PCl_3	Cl—Cl	—		3.18	5	pyramidal
PCl_3	P—Cl	—		2.04	5	
cis-CHCl·CHCl	Cl—Cl	3.6+0.1	1			
trans-CHCl·CHCl	Cl—Cl	4.7+0.1	1			
$CH_3 \cdot CHCl_2$	Cl—Cl	3.0+0.1	1			
$CH_2Cl \cdot CH_2Cl$	Cl—Cl	4.4+0.1	1			*trans* favored
CS_2	S—S	3.05+0.1	1	3.20	4,5	linear
CO_2	O—O	2.2 +0.1	1	2.25	4,5	linear
SO_2	S—O	—		1.37	5	
N_2O	N—N	—		2.38	5	
Br_2	Br—Br	—		2.27	5	
Benzene	C—C	1.4+0.1	1	1.39		plane
Cyclohexane	C—C	—		1.51		bent
Cyclopentane	C—C	—		1.52		plane
Pentane	C—C	—		1.5		tetrahedral angle
Hexane	C—C	—		1.5		

[1] Debye, *Physik. Z.*, 31, 142, 419 (1930).
[2] Debye, *Z. Elektrochem.*, 36, 612 (1930).
[3] Bewilogua, *Physik. Z.*, 32, 265 (1931).
[4] Gazewski, *Physik. Z.*, 32, 219 (1931).
[5] Wierl, *Physik. Z.*, 31, 366, 1028 (1930).
[6] Wierl, *Ann. Physik*, 8, 521 (1931).

is derived from an element measured in the metallic state. The nature of the metallic link is very obscure; most physicists regard it as neither electrovalent nor covalent; but these results make it clear that whatever may be its nature, its length is practically that of a covalent link.

A remarkable relation has recently been discovered by Hume-Rothery[39] between the values of the atomic radii as determined from the elements themselves, and especially from the metals. In order to make these comparable, the distances are calculated not at the ordinary temperature but at one-half of the "characteristic temperature"[40] for each element; this correction, which involves only a knowledge of the thermal expansion of the element, seldom exceeds two or three units in the second decimal place. In any periodic group the atomic radii of course increase with the atomic number, and the magnitude which Hume-Rothery selects for comparison is the interatomic distance d (at $\theta/2^\circ$) divided by n, the principal quantum number of the outermost group of the core, *i.e.* one less than that of the valency electrons: thus for the first short period (Li – F), $n = 1$, for the second 2, for the first long period 3, and so on. If the logarithm of d/n is plotted against the logarithm of Z, the atomic number, he shows that the values for all the elements of any one periodic group (at any rate among all but the latest groups) lie on a straight line with extraordinary accuracy, the deparature, except for certain irregularities connected with the Goldschmidt co-ordination number, seldom exceeding 1 per cent.[41] Thus we can express the relation by the general formula:

$$d/n = (1/aZ)^x$$

where x is a constant which is the same for groups with the same number of electrons in the outer electronic group of the core (inert gas type, B-metal type, transitional type) and a is another constant depending on the periodic group. Moreover for elements giving ions of the inert gas type (typical and A metals) x is very nearly 1/3, so that for these elements approximately

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[39] W. Hume-Rothery, *Phil. Mag.*, [7] 10, 217 (1930).

[40] The "characteristic temperature" is a quantity derived from the theory of specific heats. The atomic heats of all simple substances give practically identical curves if the temperature scale is expressed in terms of the ratio T/θ, where T is the temperature and θ that temperature at which the average oscillational energy of the atoms is equal to one oscillational quantum. θ, a constant for each element, is the "characteristic temperature." Thus for carbon $\theta = 1860^\circ$, for copper 315°, for sodium 172°, and for lead 88°.

[41] The theoretical values obtained from these straight lines are given in Table XIX.

$$d^3/n^3 = 1/aZ$$

For other types of elements x is larger, but not much, the maximum value being 0.42: so that on the logarithmic graph the lines of the various groups are nearly parallel.

Equally remarkable relations hold when we compare the elements in any one period. Here too, on the logarithmic plot the points lie on straight lines: but whereas the straight lines for the individual groups were found to be nearly parallel (x varying but slightly), those for the different periods have markedly different slopes, and moreover their tangents are very nearly whole numbers. Thus for the first short period the distances (in all but the latest groups) are proportional to $1/Z$ (values of $d \times Z$ are: Li, $3.02 \times 3 = 9.06$; Be, $2.29 \times 4 = 9.16$; C, $1.54 \times 6 = 9.24$). In the second short period they are proportional to $1/Z^2$ (d for Na, Mg, Si, is 3.67, 3.20, 2.35 resp.; ratio 1.56 : 1.36 : 1, and the ratio of the inverse squares of 11, 12, 14 = 1.62 : 1.36 : 1). In the third period they are proportional to $1/Z^3$ (d for K, Ca, Ti, is 4.54, 3.91, 2.95 resp.; ratio 1.54 : 1.33 : 1, and the ratio of the inverse cubes of the atomic numbers 19, 20, 22 = 1.55 : 1.33 : 1). In the fourth period, however, it is not the fourth power of Z that has to be taken but the fifth (d for Rb, Sr, Zr, is 4.85, 4.26, 3.23 resp.; ratio 1.50 : 1.32 : 1, and the ratio of inverse fifth powers of 37, 38, 40 = 1.48 : 1.29 : 1). It will be noticed that in all periods except the first, the ratio of the distances in the different groups is nearly the same:

Group		I	II	IV
Period	1	1.96	1.49	1
	2	1.56	1.36	1
	3	1.54	1.33	1
	4	1.50	1.32	1

The values obtained by Hume-Rothery for the constants x and a of his equation, are given in Table XXII.

These relations are so far unexplained; but they are so simple and exact that they must be due to some fundamental principle of atomic structure.

TABLE XXII

Constants of the Hume-Rothery Equation

Periodic Group	x	$a \times 100$
O	0.348	2.74
I, A	0.344	1.57
II, A	0.35	2.27
IV, A	0.345	4.66
V, A	0.368	6.28
VI, A	0.376	6.75
VIII, A	0.404	6.00
VIII, B	0.418	5.69
VIII, C	0.39	5.81
I, B	0.393	5.11
IV, B	0.33	5.88
V, B	0.323	4.74
VI, B	0.21	9.44

In considering the dimensions of the covalent link it would seem natural, after discussing the interatomic distances and the effective atomic radii, to proceed to the volume relations. In the solid state, as we have seen, the molecular volumes have no meaning unless they are interpreted with reference to the crystal structures. In the liquid state we might expect simpler relations to hold. So far, however, the efforts which have been made to discover such relations have had little success. The work of Kopp, Traube, and others has brought to light certain interesting relations among organic compounds, but no really satisfactory generalizations have been established. Two serious difficulties stand in the way. There is first the question of comparable temperatures. Kopp measured the densities at the boiling points, Traube at 15°. The proper course would be to measure them at the same fraction of the critical temperatures: these are comparable temperatures so far as the equation of state is accurate, which however is not strictly true. For this reason Kopp's method is better than Traube's, since the critical pressures of most organic substances do not differ very widely, and they are thus not far from being equal multiples of one atmosphere. The second difficulty is to allow for the effect on the volume of the internal pressures of the liquids. The existence of this pressure, which is manifested in the surface tension, is indisputable, and its magnitude is certainly large; but the attempts which have been made to determine it[42] have not had any great quantitative success. If it could be determined accurately, and if further the compressibilities of a sufficient number of substances were known, which is far from being the case at present, we might be able to calculate the true molecular volumes under zero pressure.

To eliminate the temperature effect, Biltz[43] and Sugden[44] have made use of an empirical relation between the temperature and the volume to calculate the molecular volumes at the absolute zero. The results agree fairly well with the values obtained by the addition of a series of terms for the atoms and linkages contained in the molecule. But their exact meaning is uncertain, and the agreement is not so good as that shown by the values of another function devised by Sugden, the parachor. This quantity is intended to overcome both the difficulties mentioned above: the effects of temperature and internal pressure. It has been shown experimentally[45] that if γ is the surface tension of a liquid, and D and d the densities in the liquid and vapor states, respectively, at the same temperature, then:

$$\frac{\gamma}{(D-d)^4} = C$$

C being independent of the temperature. Sugden's parachor[46] is the product of the molecular weight and the fourth root of Macleod's constant:

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[42] See, for example, Joel Henry Hildebrand, *Solubility* (New York, 1924), 206 p. (Amer. Chem. Soc. Monograph Series No. 17).

[43] Biltz, *Nachr. Ges. Wiss. Göttingen, Math-Physik. Klasse*, **1926**, 45; *Ann.*, **453**, 259 (1927).

[44] S. Sugden, *J. Chem. Soc.*, **1927**, 1780, 1786.

[45] Macleod, *Trans. Faraday Soc.*, **19**, 38 (1923); the same relation was deduced on (rather doubtful) theoretical grounds by R. D. Kleeman, *Phil. Mag.*, [6] **19**, 783 (1910); *ibid.*, [6] **21**, 92 (1911).

[46] S. Sugden, *J. Chem. Soc.*, **125**, 1185 (1924).

$$P = \frac{M\gamma^{\frac{1}{4}}}{D-d}$$

This is practically the molecular volume multiplied by the fourth root of the surface tension; it may be regarded as the molecular volume measured at uniform internal pressure. It has the great advantage that it is independent of the temperature, as has been verified experimentally for numerous substances over a considerable temperature range.

This magnitude proves to be in a high degree additive: the values for a substance can be expressed with great accuracy as the sum of a series of terms for the constituent atoms, with a limited number of other terms for multiple links or rings. It has already been of service in deciding questions of structure in organic compounds, and its future development may be expected to be of great value. At present however the bearing of the results is often obscure; in particular, the effects of changes of valence and of covalence do not seem to be understood. Sugden has developed a theory, involving the frequent assumption of one-electron links, indistinguishable in properties from the ordinary two-electron links, by which he claims to explain the experimental conclusions; but this theory often leads to structures which do not appear to be in accord with the chemical evidence or with the conclusions of wave mechanics.[47] A fundamental difficulty is that the real physical meaning of the parachor is unknown. I therefore do not propose to discuss the results in detail here, especially as they have been fully dealt with elsewhere.[48]

On the whole it seems that our knowledge of the effect of the covalent link on the volume of the molecule has not reached the point at which its physical implications can be usefully discussed.

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[47] See L. Pauling, *J. Am. Chem. Soc.*, 53, 3229, note (1931).

[48] S. Sugden, *The Parachor and Valency*, London, 1930. A tabulated list of all parachor values hitherto calculated is given in Landolt-Börnstein *Physikalisch-chemische Tabellen*, Ergänzungsband II (Berlin, 1930), pp. 172–188. A complete list for all substances whose surface tensions are known with sufficient accuracy is published in *Brit. Assocn. Advancement Sci. Report*, 1932, 264. For other views on the parachor see S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc.*, 1929, 2114; A. Sippel, *Ber.*, 63, 2185 (1930).

CHAPTER IV

HEATS OF FORMATION OF COVALENT LINKS

THE energy required to separate an electron from an atom—to ionize the atom—can be found from the spectrum, and is known for practically all the elements. The energy change which accompanies the sharing of a pair of electrons between two atoms in the covalent link is a magnitude of equal importance for characterizing the link, and is a factor in determining the thermodynamic stability of all molecules in which it occurs. In order to ascertain its value we must know the difference in energy between the separate atoms and the molecule in which they are linked, or the energy of formation of the molecule from its atoms. The existing thermochemical data enable us to calculate the heats of formation of an enormous number of compounds from their elements. For example, for many organic compounds of carbon, hydrogen, oxygen and nitrogen we know the heats of combustion, that is, of conversion into carbon dioxide, water, and nitrogen gas; we also know the heats of formation of carbon dioxide and water from solid carbon, oxygen gas and hydrogen gas. If we further know the heats of dissociation of solid carbon and these three elementary gases into their atoms, we can calculate the energy evolved in the formation of a molecule of any of these substances from its constituent atoms.

With diatomic molecules this gives us immediately the value we need, but it is obvious that many of the links in which we are interested, such as C—H and O—H, occur only in more complicated molecules. In such cases the heat of formation tells us the sum of the energy values for several links. As a first approximation we can assume that the energy of a link is, as a rule, but little affected by the other links in the molecule; that the heat of formation of a molecule from its atoms is an additive property: it is the sum of a series of approximately constant values for the several links which the molecule contains. With this as a working hypothesis we can extend our investigation to a very great variety of linkages. One of the first to draw attention to the subject was Fajans,[1] when he showed that the heat of the C—C link was almost exactly the same in diamond as in a paraffin. The subject was further examined by Von Weinberg, Eucken, Grimm and Wolff, and others;[2] but its full investigation has become possible only in recent years, because the necessary values of the heats of atomization, our knowledge of which largely depends upon the application of modern spectroscopic methods, have been only recently ascertained.

HEATS OF ATOMIZATION

When a reaction can be carried to completion under realizable conditions, the heat evolved can be measured directly. It is in this way, of course, that the heats of combustion of substances are determined. But the heats of conversion of the elements from their ordinary forms into the fully dissociated (atomized) vapor cannot usually be measured in this way.[3] We can, however, sometimes measure it by observing the change of dissociation with temperature, making use of the Clausius-Clapeyron equation relating this change to the heat of dissociation. This has been done, for example, for chlorine, bromine, and iodine. The degree of dissociation can be measured by means of the pressure, and in other ways. For this purpose the molecular-beam method has been used.[4] When the atom has a magnetic moment and the molecule has not, as with the diatomic molecules of the alkali metals and bismuth, the atoms alone are deflected in an inhomogeneous magnetic field, as in the original experiments of

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[1] K. Fajans, *Ber.*, 53, 643 (1920); *ibidem*, 55, 2826 (1922). See also Von Weinberg, *Ber.*, 53, 1347 (1920).

[2] References are given on page 97, etc. The results were summarized by Grimm in Geiger and Scheel, *Handbuch der Physik* (Berlin, 1926), vol. 24, p. 532, and are quoted and briefly discussed by Eucken, *Lehrbuch der chemische Physik* (Leipzig, 1930), p. 880. The numerical values need some modification in the light of later determinations of the heats of atomization.

[3] See, however, Rodebush and Troxel, *J. Am. Chem. Soc.*, 52, 3467 (1930); Copeland, *Phys. Rev.*, 36, 1221 (1930).

[4] See Chapter V, page 135.

Stern and Gerlach. They can then be collected separately on a plate, and their relative amounts approximately determined.[5] The variation of the proportions with temperature then gives the heat of dissociation. It is also possible to determine the proportions of atoms and molecules from the spreading of a rapidly rotating molecular beam.[6]

These methods are, however, only applicable with any degree of accuracy to relatively few elements. As a rule we have to rely on the observation of the spectra.[7] There are three possible spectroscopic methods by which the energy of dissociation of a molecule might be measured:

(1) The molecule might be bombarded by electrons of increasing energy, and the voltage required for its dissociation observed;

(2) The rotational energy of the molecule might be increased by thermal or electrical excitement, until the centrifugal force was sufficient to dissociate it;

(3) The vibrational energy either of the normal or of the excited molecule might be increased until it was large enough to make the atoms separate.

The first two methods cannot at present be applied with sufficient accuracy to be of quantitative value, although the results afford an important confirmation of the general theory. Some excited molecules, instead of dissociating immediately on absorption, show the phenomenon of predissociation. This consists in a fusion of the rotation lines within the vibrational bands, and is probably due to the formation of unstable molecules which dissociate into two atoms or residues.[8] It can be shown that the corresponding energies are greater, but not much greater, than those required to break the links. The predissociation thus gives an approximate value of the energy of dissociation.

[5] Leu, *Z. Physik*, **49**, 498 (1928); Lewis, *ibidem*, **69**, 786 (1931).

[6] Zartman, *Phys. Rev.*, **37**, 383 (1931).

[7] R. T. Birge, "Molecular Spectra in Gases," *Bull. Natl. Research Council*, 11 (1926); H. Sponer, "Optische Bestimmung der Dissoziationswärme von Gasen," *Ergebnisse exakte Naturw.*, 6 (1927); *Z. Elektrochem.*, **34**, 483 (1928); R. Mecke, *Bandspektra und ihre Bedeutung für die Chemie* (Berlin, 1929), p. 44; Herzberg, "Die Prädissoziation und verwandte Erscheinungen," *Ergebnisse exakte Naturw.*, 10 (1931); E. Rabinowitsch, *Z. Elektrochem.*, **37**, 91 (1931). The complete literature is quoted in Landölt and Börnstein, etc., *Physikalisch-chemische Tabellen*. . . .(Berlin, 5th Ed., 1931), 2te Ergänzungsband, p. 1614ff.

[8] K. F. Bonhoeffer and L. Farkas, *Z. physik. Chem.*, **134**, 337 (1928); Herzberg, "Prädissoziation . . .," *Ergebnisse exakte Naturw.*, 10 (1931).

The rotational energy required for disruption is certainly greater, and sometimes considerably greater, than the vibrational; for example, with the molecule HgH the rotational energy required is 14.3 kgm-cal while the vibrational is only 8.5 kgm-cal, which must mean that when the atoms fly apart through centrifugal force they possess considerable kinetic energy. But we cannot yet calculate the amount of this excess of energy, and so we cannot use this method for determining the energy of the dissociation itself.

The third method, that of observing the oscillational or vibrational energy required to disrupt the molecule, is the one actually employed. This was first suggested by Franck,[9] and applied in particular to the halogens. The successive vibrational lines of a band system—like those of a series in an atomic spectrum—converge to a limit. If the band spectrum can be observed as far as the limit, it is found that at this point the bands are replaced by a continuous spectrum. With an atomic spectrum the limit of a series indicates the point at which the excited electron separates wholly from the atom, and ionization occurs. With a band spectrum the convergence point is that at which the atoms separate from one another, and so it gives us the energy of dissociation. The continuous (absorption) spectrum is due to the fact that if the energy of the light is sufficient to disrupt the molecule, any further quantity of energy can be absorbed as kinetic energy of the dissociated atoms; and as this kinetic energy is not quantized the absorption becomes continuous. In principle, then, the method is simple. The absorption spectrum of the gas in question is measured, and the limit of the band system, at which the bands pass into a continuous absorption, is either observed directly or calculated from the formula of the band system. This gives us the wave length, and hence the energy, of the light required to dissociate the molecule.

There are, however, certain difficulties. It is not always possible to observe a sufficient number of lines of the band system to extrapolate with certainty to the limit. A more serious difficulty arises from the fact that what we want to know is the energy required to convert a normal unexcited molecule into normal unexcited atoms. We must therefore be able to ascertain that the state from which our band system starts is a normal state of the molecule, or if it is not, we must determine how far its energy level lies above that of the normal state. Also we must know the state of the resulting dissociated atoms. At the limit of the band spectrum their kinetic energy is zero; but it is found that commonly the photodissociation of a covalent molecule produces two neutral atoms, one in a normal and the other in an excited state; this is, in fact, a criterion of the covalent link (see page 56). This does not prevent the method from being applicable, but it makes it necessary to identify correctly the states of the dissociated atoms and to know the amount by which their energy exceeds the normal. This identification can sometimes be effected through an approximate determination of the energy of normal dissociation—into unexcited molecules—by means of methods that are less accurate but are not subject to this uncertainty as to the excitation of the products of dissociation.

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[9] J. Franck, *Z. physik. Chem.*, 120, 144 (1926).

The way in which these rather complicated corrections are applied will be found in works on band spectra, such as that of Mecke.[7] It is enough to say here that they make it possible to determine the heats of dissociation into atoms of the elements in which we are most interested, with a possible error sometimes less than 1 per cent (0.3 to 1 kgm-cal per gram-atom). The rapid progress of spectroscopy will, no doubt, soon lead to an increase in both the number and the accuracy of these results. At present we have to do the best we can with the data available. It should be observed that many of the conclusions to be derived from a knowledge of the heats of rupture of covalent links depend rather on their relative than on their absolute values, and that these will be less affected by errors in the absolute values of the fundamental heats of atomization.

These methods of measuring the heats of atomization are, of course, applicable to compound molecules as well as to elements. Where the compound molecules are diatomic they give the heat of formation of the link directly; where they are polyatomic, if the products of dissociation are single atoms, they give the sum of the heats of formation of all the links in the molecule. But when the polyatomic molecule splits off one of its atoms, the energy absorbed is not necessarily the normal energy of the link. For example, Mecke's results[10] show that the heat of dissociation of water into its atoms is 217 kgm-cal, so that the value for a single O—H link in water is half of this, or 108.5 kgm-cal. But for the dissociation of the OH molecule 123 kgm-cal are required. Hence the heat of the reaction:

$$\text{H—O—H} \longrightarrow \text{H} + \text{O—H}$$

is 94 kgm-cal. Thus we have three different values for the heat of formation of an O—H link. Of these, it is clear that the "normal" value is the first, 108.5, since the other two depend upon the energy content of the abnormal intermediate molecule OH. The knowledge that these experiments give us concerning the properties of such abnormal molecules, is in itself of course of great interest.[11]

The most accurate values for the heats of atomization of the more important elements are given in Table XXIII.

TABLE XXIII

Heats of Atomization of Elements

(In kilogram-calories per gram-atom)

Element	State	Heat of Atomization
Hydrogen	gas	51.5
Oxygen	gas	59
Nitrogen	gas	104
Carbon	solid	150
Fluorine	gas	32.0
Chlorine	gas	28.7
Bromine	gas	24.9
	liquid	28.7
Iodine	gas	18.0
	solid	25.5
Sulphur	S_2 gas	52.0
	rhombic	66.8

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[10] R. Mecke, *Z. physik. Chem.*, B7, 108 (1930).

[11] See G. Scheibe, *Z. physik. Chem.*, B5, 355 (1929); G. Herzberg and G. Scheibe, *ibidem*, B7, 390 (1930).

HEATS OF COMBUSTION

The majority of the links with which we are concerned occur in organic compounds, and for these we require to know heats of combustion of those compounds. The technique of the measurements need not be discussed here, but we have to consider exactly what information they give us and how far they need correction for our purposes. The thermo-chemical data are taken mainly from the *International Critical Tables* and from the extensive list given by Kharasch.[12]

Since we are concerned to determine the properties of molecules as free as possible from the influence of their surroundings, the heats of formation or of rupture should strictly be measured at zero pressure and at the absolute zero of temperature. The correction for pressure, which involves the van der Waals force, is not serious, and we may use the observed values which are corrected for constant pressure; the spectroscopic data are obtained at constant volume and so must be corrected for constant pressure, by the addition of RT which is 0.6 kgm-cal at 300°Abs. The correction from a temperature of 20°C, to which the thermochemical data are referred, to 0°Abs involves more knowledge of the specific heats at low temperatures than we usually possess, and for practical purposes we have to be content with the values at 20°. Heats of combustion are normally obtained at this temperature; that is to say the bomb starts from and returns to it. When the substance used is a gas no further correction is needed; but when it is a liquid or a solid we must allow for the heat required to convert it into vapor. To form an estimate of the extent of these corrections, we may consider what they amount to for the substances chiefly concerned, which are volatile compounds of the lighter elements and largely organic.

The possible errors in the fundamental values are, in a sense, less important than those in the heats of combustion, because they affect alike all the links in which the particular element is concerned: thus an error in the heat of volatilization of carbon would have the same effect on all the links in which one atom is carbon, but it would not alter their differences (see page 109). The heats of combustion of organic substances are of the order of 200–2000 kgm-cal per gram-molecule. Their accuracy is, of course, very variable, but in the better work may be taken to be between 1 and 0.1 per cent—for an average value of 1000 kgm-cal, say from 1 to 10 kgm-cal. The effect of this on the value obtained for the heat of rupture of a particular link will depend upon how large a part the energy of this link is of the heat of formation of the whole molecule. When, as often happens, we are investigating a linkage that only occurs once in the molecule any error in the total heat will fall wholly on this particular value.

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[12] M. S. Kharasch, *Bur. Standards J. Research*, 2, 359 (1929).

The heats of rupture of individual links are usually between 40 and 150 kgm-cal. The differences found in the value for a particular link according to the compound selected, which are due to the combined effect of the errors of measurement and the departure of the molecular heats from strict additivity, seldom exceed 10 per cent, and are often much less. Thus in arriving at these values it is important to eliminate as far as possible any errors exceeding 1 or 2 kgm-cal.

The heats of fusion of organic compounds are usually between 4 and 7 kgm-cal, and are seldom less than 2 or more than 10. The heats of evaporation are, on the whole, larger and vary with the boiling point; they amount to about 7 kgm-cal for a non-associated substance boiling at 50°, and about 12 for one boiling at 250°; associated substances give values up to 20 or 30 per cent larger. Speaking roughly, therefore, we may say that the neglect of either the heat of fusion or that of evaporation may cause an error (of excess) in the value for the linkage of about 10 per cent. It is therefore obviously necessary that these quantities should be known and allowed for, although we do not need to know them with very great accuracy. For the heat of fusion, where the substance is a solid, we have no general method of calculation; unless we are to be content with a guess of 5 or 6 kgm-cal, this must be measured. Many organic solids have been used as solvents in cryoscopic work, and in that event their heats of fusion have been determined, or can be calculated from the cryoscopic constant by means of van 't Hoff's equation. The heats of evaporation, which we need much more generally, have for some substances been determined or can be calculated from the vapor-pressure curve. Where, as is more often the case, this is unknown, we can get a sufficiently accurate value by means of Trouton's rule, if the boiling point is known. This rule states that the molecular heat of evaporation is 21 times the absolute boiling point at atmospheric pressure. For a substance whose boiling point is known or can be measured only under reduced pressure, the value at atmospheric pressure may be estimated by comparison with some similar compound (Ramsay-Young rule). A more accurate form of Trouton's rule is that given by Von Wartenberg:[13]

$$\text{Heat of evaporation} = 7.4T \times \log T$$

where T is the temperature of the absolute boiling point under atmospheric pressure. Two examples, chosen at random, may be given to show the accuracy of these rules.

Substance	Boiling point	Heat of Evaporation		
		Obs.	Calculated	
			Trouton	Von Wartenberg
Acetaldehyde	21°C	6.0	6.2	5.4
Naphthalene	218°	9.7	10.3	9.8

It will be seen that the values obtained by the second rule lie very close to the truth; and it is easy to draw a curve from which the heat corresponding to any boiling point may be read off. This rule applies to non-associated substances; associated substances, as has been said, give values that may be 20 or even 30 per cent higher, but here an approximate allowance can be made.

Even now, however, the corrections are not quite complete. The values of the latent heats obtained by these methods are those which hold at the melting and the boiling points respectively. We want to know the values at 20°. If the molecular heats of solid and liquid, or of liquid and gas, are known, these values can be calculated, since the temperature coefficient of the latent heat is the difference between the molecular heats of the two phases.

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[13] Von Wartenberg, *Z. Elektrochem.*, 20, 444 (1914).

Usually, however, these have not been determined. From those that have we can form an estimate of the magnitude of the effect. Van 't Hoff showed[14] that the specific heat of a substance is always less in the solid than in the liquid state, and this has since been recognized as following from the Nernst theorem. The heat of fusion must, therefore, diminish with a fall of temperature. The effect however is small. In a list of 13 organic substances quoted by van 't Hoff, the difference scarcely ever exceeds 0.02 kgm-cal per degree and the average is 0.013. For anthracene and triphenylmethane Hildebrand found 0.009 and 0.016, respectively.[15] Narbutt[16] examined the isomeric dichloro-, dibromo-, diiodo-, and chlorobromobenzenes (11 compounds) and found the maximum difference to be 0.016 and the mean 0.013 kgm-cal. Hence, for a substance melting at 200° (and since for our purposes the boiling point of the substance must be known, we shall not, as a rule, meet with melting points higher than this) the fall in the latent heat would be unlikely to exceed 3.5 kgm-cal, and on the average, would be 2.3 kgm-cal. With a melting point of 100° the extreme value would be 1.5 and the average about 1. This is practically within the limits of experimental error, unless the melting points are unusually high, when some allowance can be made.

In the latent heat of evaporation the change with temperature is in the opposite direction, the specific heat of the liquid being the greater. The following values, taken from the *International Critical Tables*, show the change of latent heat in kgm-cal per degree:

Non-associated		Associated	
Isobutane	0.014	Water	0.010
n-Hexane	0.012	Ammonia	0.011
Benzene	0.013	Sulphur dioxide	0.023
CCl_4	0.011	Methyl alcohol	0.010
$CHCl_3$	0.012	Ethyl alcohol	0.010
Ether	0.018	Propyl alcohol	0.018
Acetone	0.011		

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[14] Van 't Hoff in *Boltzmann Festschrift* (1904), p. 233.

[15] J. H. Hildebrand, A. D. Derschak, A. H. Foster and C. W. Beebe, *J. Am. Chem. Soc.*, 39, 2293 (1917).

[16] J. Narbutt, *Z. Elektrochem.*, 24, 339, 342 (1918).

The mean value of the temperature coefficient is 0.013, remarkably close to that for the latent heat of evaporation, and it practically never exceeds 0.018. Thus the mean and the maximum corrections to 20° for the latent heat of evaporation of substances with various boiling points would be:

Boiling point		100°	200°	300°
Correction (in kgm-cal)	mean	+1.0	+2.4	+3.7
	maximum	+1.4	+3.2	+5.0

It is thus clear that this correction is just large enough to be worth introducing, but that it is sufficient to use the mean values; and the Von Wartenberg curve relating the heat of evaporation to the boiling point should be corrected accordingly.

As a concrete example to show the magnitude of these subsidiary terms we may take naphthalene, which melts at 80° and boils at 218°. The heat of combustion, Q, according to recent data, is 1231.8 kgm-cal with an uncertainty of less than 0.5 kgm-cal; it is of course much better known than most. That of the carbon and hydrogen which it contains, in the solid and gaseous states respectively, is 1217.3. Hence the heat of formation H_f of the solid is -14.5 kgm-cal. The heat of atomization of these elements in these quantities is 1912 kgm-cal, and so the heat of formation of solid naphthalene at 20° from its component atoms is $1912-14.5=1897.5$ kgm-cal. We have to find the value for the vapor at this temperature, and so to subtract the heat required to convert one kilogram-molecule of the solid at 20° into the vapor at 20°. The heat of evaporation at the boiling point has been found to be 9.66, and that of fusion at 80° 4.56, giving a total of 14.22 kgm-cal. We have still to allow for the changes in the latent heats on going from the boiling or melting points to 20°. For the evaporation this will involve a rise of $198 \times 0.013 = 2.57$ as a mean, or $198 \times 0.018 = 3.56$ as a maximum. The heat of fusion will fall by $55 \times 0.013 = 0.7$ on the mean or $55 \times 0.02 = 1.1$ as a maximum. The corrected values for the latent heats will thus be, on the mean, 14.22 + 2.57 − 0.78 = 16.01 with an uncertainty of about 1 kgm-cal, which is certainly less than the errors of determinations of the heat of combustion for most substances. The final value for the atomic heat of formation of naphthalene is thus 1897.5 − 16.0 = 1881.5, and the error in the deduced value of any single linkage in such a compound will be about 1 or 2 units in a value of the order of 100.

RESULTS

Some examples may be given of the application of these values to the calculation of the heats of rupture of covalent links.

Heats of combustion are normally referred to 20° and constant pressure. To find the heat of formation of a compound from its elements in their normal state, we have to subtract the heat of combustion of the compound from that of its component elements. The relevant reactions are:

$$\begin{aligned} &C_{\text{solid}} \rightarrow CO_2 \\ &H_{2\,\text{gas}} \rightarrow H_2O \\ &F_{2\,\text{gas}} \rightarrow HF \\ &S_{\text{solid}} \rightarrow SO_2 \end{aligned}$$

Of the other elements commonly present oxygen, nitrogen, chlorine, bromine and iodine usually separate in the elementary state, and if so need not be brought into the account. The heats of the above mentioned reactions being known, the heat of formation H_f from the elements in their ordinary states of a compound $C_aH_bF_cS_d$ with any amount of oxygen, nitrogen, chlorine, bromine or iodine (where of course any of the numbers a,b,c,d may be zero) is given by the equation:[17]

$$H_f = -Q + 94.38a + 34.19b + 75.6c + 69.3d$$

of course where Q is the heat of combustion (all the values being in kilogram-calories).

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[17] See *International Critical Tables* (New York, 1929), Vol. 5, p. 162.

Example I:

$$\begin{aligned} &\mathrm{CH_{4\,gas}},\quad Q = 212.7, \\ H_f &= -212.7 + 94.38 \times 1 + 34.19 \times 4 \\ &= -212.7 + 231.2 \\ &= +\ 18.5 \end{aligned}$$

To obtain the atomic heat of formation, H_a, we must add the heats of atomization of 1C and 4H, or $150 + 4 \times 51.5$, giving:

$$\begin{aligned} H_a &= 18.5 + 356.0 \\ &= 374.5 \end{aligned}$$

Example II:

$$\begin{aligned} &\mathrm{C_2H_{6\,gas}},\quad Q = 368.3 \\ H_f &= -368.3 + 2 \times 94.38 + 6 \times 34.19 \\ &= +\ 25.6 \\ H_a &= 25.6 + 2 \times 150 + 6 \times 51.5 \\ &= 634.6 \end{aligned}$$

If we write x for the heat of rupture of the link C—H, and y for that of C—C, we have:[18]

$$\begin{aligned} 4x = 374.5 \text{ and } x &= 93.6 \\ 6x + y &= 634.6 \\ 6x &= 561.6 \\ y &= 73.0 \end{aligned}$$

This is, of course, on the assumption that the heat of rupture of the C—H link is the same in both compounds. This assumption can be tested more generally, and in a way that is independent of the accuracy of our heats of atomization. If the C—C and C—H links have the same values in all paraffins, then in passing from one homologue to the next higher, there must always be the same change in all three heats, Q, H_f and H_a. The value of H_a will depend upon those assumed for the heats of atomization, but the values of Q and H_f will not. In Table XXIV are given the values of Q for the normal paraffins, those for liquids being corrected for the heats of evaporation.

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[18] More accurate values are given later.

The agreement is good. The effect of the addition of CH_2 appears to be constant, within the normal limits of the experimental error.

These methods enable us to determine the heats of rupture of a series of links in organic compounds. By comparing a sufficient number of substances we can discover how far the values are really independent of the nature of the rest of the molecule. The investigations of Grimm show that certain constitutive differences influence the values considerably; the values for C—X, where X is carbon, nitrogen, oxygen or a halogen, differ according as the carbon is part of an aliphatic or of an aromatic radical. But apart from such special influences, it would appear that the additive relation holds within a limit of error of about 5 per cent, which is small when we consider how uncertain some of the thermochemical data are.

TABLE XXIV

Heats of Combustion, Q, of Normal Paraffins

Number of Carbon atoms	$Q_{\text{corr.}}$	Differences	
1	212.7	155.6	156.8
2	368.3	158.0	
3	526.3	157.1	
4	683.4	155.9	157.8
5	838.3	159.5	
6	997.8	159.7	157.6
7	1157.5	155.5	
8	1313.0		
Mean of seven,			*157.2*

Before we come to deal with the links in general, we may consider two that are of fundamental importance: the link of carbon to carbon and that of carbon to hydrogen.

For determining the heat of formation of any link that occurs in organic compounds it is necessary, of course, to know the heat of atomization of carbon, and unfortunately this is very difficult to ascertain. The method first used was to measure the temperature of the carbon arc burning at various pressures. This may be taken to be the temperature at which the vapor pressure of carbon is equal to that of the surrounding atmosphere, and so a knowledge of its variation with the pressure gives us the heat of volatilization which, if the vapor may be assumed to be monatomic, is the heat of atomization. The difficulty is to obtain accurate data. The earlier values obtained in this way were much too large, but subsequently Kohn[19] redetermined the temperatures, and obtained a mean value of 163 kgm-cal per gram-atom. There is no doubt that the heat of the reaction: $C_{solid} \rightarrow C_{gas}$ is in the neighborhood of 150 kgm-cal.[20] Mecke adopts the value 141; Grimm gives 150 in his tables; Haber[21] adopts 140. The value used here is 150.

If we assume this value, together with that of the atomization of hydrogen (51.5 kgm-cal per gram-atom) which is much more certain, we can calculate the heats of C—H and C—C, as we have seen, from the heats of combustion of any two paraffins. That of C—H is one-fourth of the heat of formation of methane, of which the heat of combustion is accurately known. By combining this with the heat of formation of a molecule C_nH_{2n+2}, which contains $(n-1)$ C—C and $(2n+2)$ C—H links, we arrive at the value for C—C. A more accurate way is to calculate this for several paraffins and take the mean.[22]

The values that give the best agreement for the paraffins are: C—H = 93.61, C—C = 71.14. Table XXVI (page 111) gives, for a series of saturated paraffins, the observed values of the heats of formation and those calculated on this hypothesis.

These values of the C—H and the C—C links in aliphatic radicals are used throughout. That they cannot be very greatly in error is shown in various ways. In the first place, the heat of evaporation of diamond itself gives us a measure of the heat of rupture of the C—C link. We know that every carbon atom in diamond is attached to four others by single links, and since these links are of the same length as those in the paraffins and like them are arranged tetrahedrally, we should expect that their heats of rupture would be much the same. If we suppose *N* carbon atoms to evaporate from the diamond, each will break four C—C links; but as each of these links involves two carbon atoms the total number broken will be 2*N*. Thus the heat of evaporation should be about twice the heat of rupture of a C−C link. We have found the latter to be 71.1 kgm-cal, and the former to be 150, so that this condition is very nearly fulfilled. Since this agreement does not depend upon the particular value[22] adopted for the heat of atomization of carbon, it provides independent evidence of the correctness of the assumed heat of rupture of C−H.

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[19] H. Kohn, *Z. Physik*, 3, 143 (1920). See K. Fajans, *Ber.*, 53, 643 (1920); *ibidem*, 55, 2826 (1922). See however W. E. Vaughan and G. B. Kistiakowsky, *Phys. Rev.*, (ii) 40, 457 (1932).

[20] The heat of combustion and hence the energy content of diamond is only 0.2 kgm-cal per gm-atom larger than that of graphite, so that it makes no sensible difference which we take as our reference substance.

[21] K. F. Bonhoeffer and F. Haber, *Z. physik. Chem.*, 137, 263 (1928).

[22] It can easily be shown that if the value we use for the heat of atomization of carbon is x units too low, the value obtained for C—H will be $0.25x$ too low and that for C—C will be $0.5x$ too low. In general, an error of x in the heat of atomization of any element causes an error of x/n in that of any link of which this element forms a part, where n is the valence of the element.

Again, approximate values of the heats of rupture of several of these links can be obtained: (1) from extrapolation of the infra-red band spectra; and (2) from the observation of predissociation. The former probably, and the latter certainly represent upper limits. These are entirely independent of the heats of atomization of the elements. In Table XXV (below) the values so obtained are compared with those calculated from the thermochemical data. We

TABLE XXV

Heats of Rupture of C—H *and* C—C *Links*

(al = aliphatic, ar = aromatic)

Link	Obs.	Substance	Method
C_{al}—H	97 ± 5	Hexane	Infra-red
Calc. 93.61	94 ± 5	Cyclohexane	Infra-red
	93 —	Acetaldehyde	Predissociation
C_{ar}—H	117 ± 6	Benzene	Infra-red
Calc. 101.73	117 ± 6	Aniline	Infra-red
	110 —	Benzaldehyde	Predissociation
C—C	88 —	Acetone	Predissociation
Calc. 71.14	88 —	Crotonaldehyde	Predissociation

are justified, therefore, in concluding that the values we have obtained are not far from the truth.

The thermochemical data for the hydrocarbons are given in Tables XXVI to XXIX (pp. 111–113). The heats of formation from the atoms, H_a, are obtained from the heats of combustion, Q, assuming 150 and 51.5 as the heats of atomization of solid carbon and of gaseous hydrogen, respectively. The results show that the heat of formation of the link C—C or C—H is different according as the carbon forms part of an aliphatic or of an aromatic radical. A similar difference is found with the dipole moments of links, but not, so far as is known, with their dimensions. The values that give the best agreement with observation are:

C_{al}—C_{al}	71.14	C_{al}—H	93.61
C_{al}—C_{ar}	79.4	C_{ar}—H	101.73
C_{ar}—C_{ar}	97.17		

The calculated heats of formation in Tables XXVI, XXVII, and XXVIII are obtained by the use of these values.

TABLE XXVI

Saturated Paraffins: Heat of Formation from Atoms

Compound	Formula	Heat of Formation		
		Obs.	Calc.	Diff.
Methane	CH_4	374.46	374.44	± 0
Ethane	C_2H_6	634.5	632.7	− 1.8
Propane	C_3H_8	891.8	891.2	− 0.6
n-Pentane	C_5H_{12}	1411.9	1407.9	− 4.0
n-Hexane	C_6H_{14}	1668.6	1666.1	− 2.5
n-Heptane	C_7H_{16}	1923.5	1924.5	+ 1.0
n-Octane	C_8H_{18}	2182.8	2182.9	+ 0.1
n-Decane	$C_{10}H_{22}$	2708.5	2699.7	− 8.8
Isobutane	C_4H_{10}	1151.0	1149.6	− 1.4
Isopentane	C_5H_{12}	1406.7	1407.9	+ 1.2
2,3-Dimethylbutane	C_6H_{14}	1672.0	1666.1	− 5.9
2,2-, 2,3-, and 2,4-Dimethylpentane	C_7H_{16}	1924.4	1924.5	+ 0.1
2- and 3-Methylhexane	C_7H_{16}	1924.3	1924.5	+ 0.2
3,3-Dimethylpentane	C_7H_{16}	1924.3	1924.5	+ 0.2
2,3,3-Trimethylbutane	C_7H_{16}	1924.5	1924.5	± 0
3-Ethylpentane	C_7H_{16}	1923.9	1924.5	+ 0.6
2,5- and 3,4-Dimethylhexane	C_8H_{18}	2184.3	2182.9	− 1.4
3-Ethylhexane	C_8H_{18}	2185.8	2182.9	− 2.9
2-Methylheptane	C_8H_{18}	2182.7	2182.9	+ 0.2
2,6-Dimethyloctane	$C_{10}H_{22}$	2702.9	2699.7	− 3.2

TABLE XXVII

Cyclic Paraffins: Heats of Formation

Compound	Formula	Heat of Formation		
		Obs.	Calc.	Diff.
3-Rings				
Cyclopropane	C_3H_6	750.5	775.1	+24.6
4-Rings				
Methyl cyclobutane	C_5H_{10}	1287.7	1291.8	+ 4.1
5-Rings				
Cyclopentane	C_5H_{10}	1288.7	1291.8	+ 3.1
Methyl cyclopentane	C_6H_{12}	1549.7	1550.2	+ 0.5
1,3-Dimethyl cyclopentane	C_7H_{14}	1811.8	1808.6	− 3.2
1,2,4-Trimethyl cyclopentane	C_8H_{16}	2072.8	2066.9	− 5.9
6-Rings				
Cyclohexane	C_6H_{12}	1548.4	1550.2	+ 1.8
Methyl cyclohexane	C_7H_{14}	1810.3	1808.6	− 1.7
1,1-Dimethyl cyclohexane	C_8H_{16}	2074.7	2066.9	− 7.8
1,2,3-Trimethyl cyclohexane	C_9H_{18}	2336.5	2325.3	−11.2
7-Rings				
Cycloheptane	C_7H_{14}	1814.2	1808.6	− 5.6
Methyl cycloheptane	C_8H_{16}	2071.8	2066.9	− 4.9
Ethyl cycloheptane	C_9H_{18}	2323.3	2325.3	+ 2.0

TABLE XXVIII

Aromatic Hydrocarbons

Compound	Formula	Heat of Formation		
		Obs.	Calc.	Diff.
Benzene	C_6H_6	1193.2	1193.4	+ 0.2
Toluene	C_7H_8	1451.0	1451.9	+ 0.9
Ethylbenzene	C_8H_{10}	1710.6	1710.3	− 0.3
o-Xylene	C_8H_{10}	1709.8	1710.3	+ 0.5
m-Xylene	C_8H_{10}	1712.0	1710.3	− 1.7
p-Xylene	C_8H_{10}	1712.7	1710.3	− 2.4
n-Propylbenzene	C_9H_{12}	1971.1	1968.9	− 2.2
Isopropylbenzene	C_9H_{12}	1970.3	1968.9	− 1.4
Mesitylene	C_9H_{12}	1975.3	1968.9	− 6.4
Naphthalene	$C_{10}H_8$	1881.5	1882.7	+ 1.2
Anthracene	$C_{14}H_{10}$	2565.4	2571.9	+ 6.5
Phenanthrene	$C_{14}H_{10}$	2565.7	2571.9	+ 6.2

The results obtained with the open-chain saturated hydrocarbons are very concordant; the differences between the observed and the calculated heats, which amount on the average to 2.5 kgm-cal, may be taken to be experimental errors. There is no indication of any progressive change with molecular weight, or of any effect of a branching of the chain. Among the cyclic hydrocarbons the effect of strain is very marked in cyclopropane, the energy of which is 24.5 kgm-cal more than that derived from the calculation. As is shown below, the heat of formation of the double link C=C is about 123 kgm-cal, or 19 kgm-cal less than that of two single links. Hence if we may take the strain in a molecule to be measured by its excess energy-content, it would appear that the strain in a 3-carbon ring is equal to, or is rather greater than that in a double link: the heats of formation of propylene (752.5) and cyclopropane (750.6) are practically identical.[23] In the cyclobutane ring there still seems to be a slight strain effect, though it scarcely exceeds the probable error. The aromatic hydrocarbons, including naphthalene, anthracene and phenanthrene, give concordant results, the mean error being less than 3 kgm-cal.

For the open-chain unsaturated compounds Table XXIX gives the values of the heats of formation of the double and triple carbon links, calculated on the as-

TABLE XXIX

Unsaturated hydrocarbons

Compound	Formula	Heat of Formation	Calculated for Link
Olefines			C=C
Ethylene	C_2H_4	499.6	125.2
Propylene	C_3H_6	752.5	119.7
Trimethylethylene	C_5H_{10}	1275.4	125.9
Isoprene	C_5H_8	1141.3	2×125.1
Amylene	C_5H_{10}	1269.6	120.1
			Mean 123.2
Acetylenes			C≡C
Acetylene	C_2H_2	348.2	161.0
Heptine-1	C_7H_{12}	1640.2	161.2
			Mean 161.1

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[23] The uncertainty as to a possible effect on the value of C—H of its carbon atom being doubly linked, is discussed below: here it is assumed that there is no such effect.

sumption that those of C—C and C—H are the same as in the paraffins. The mean values obtained from the rather scanty data are: C=C 123, and C≡C 161 kgm-cal.[24]

We have no means of checking the assumption that the heats of C—C and C—H are the same in unsaturated as in saturated compounds. But if they are not we should expect them to be larger, as they are in aromatic compounds, and in that case C=C and C≡C must be smaller than we have found them to be. If we take C—C and C—H to have the same values when one of the carbons is unsaturated as when one of them forms part of an aromatic ring, we get C=C equal to 91 and C≡C equal to 145 kgm-cal. The ratio of the heats of formation, H_a, of C—C, C=C, and C≡C, on these two hypotheses is:

	(a)		(b)	
	H_a	Ratio	H_a	Ratio
$C_{al}—C_{al}$	71	1	71	1
C=C	123	1.73	91	1.28
C≡C	161	2.26	145	2.04
$C_{ar}—C_{ar}$	97.2	1.37	—	—

It therefore seems that the first hypothesis is nearer to the truth; we can scarcely suppose that the heat of formation of a double ethylenic link is less than the mean value for the links in the benzene nucleus. This question of the relative values of the multiple carbon–carbon links is of great interest, because, although we should have expected, from the unsaturated character of the compounds, that the heat of formation would increase less rapidly than the multiplicity of the link, this appears to be true only of the link of carbon to carbon, as will be shown later; in all others, such as those of carbon to nitrogen, oxygen, and sulphur, the heat of formation is at least twice as great for a double link and three times as great for a triple link. It is, therefore, important that we can show that this exceptional behavior of the links of carbon to carbon is real and is not based on a mistaken assumption as to the effect of the unsaturation on the other links in the molecule.

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[24] Two supposed acetylene derivatives, described as allylene and *n*-hexyl acetylene, are excluded from the list. They give C≡C as 174.3 and 172.3, respectively. This suggests that the compounds examined contained not one triple but two double links. If we add to the above values that for a single C—C link we get 245.4 and 243.4; the mean value for two double links is 246.

The heats of formation of other links must be treated more briefly; but one curious and so far unexplained difficulty must be pointed out that affects all the compounds except the hydrocarbons. It is obvious, in obtaining the value for any particular link, to try to reduce the experimental errors by comparing the results given by a series of homologues. With the paraffins this method is quite satisfactory; as is shown by the list in Table XXVI, the differences between the observed and the calculated values are small and are distributed at random, being obviously due to experimental error; the mean values obtained for the links C—C and C—H are accurate to within 0.2 or 0.3 kgm-cal. But in almost every other homologous series, alcohols, esters, ketones, amines, halides, etc., it is found that the increase in the heat of formation for successive additions of CH_2 grows larger as we ascend the series; the value deduced for the particular link must, of course, increase to the same extent. As examples the values for the alkyl halides and the alcohols are given in Table XXX. This effect is independent of any calculation of the heats of formation; it appears as a fall of the heats of combustion, since these are introduced into our equation as negative quantities, and it has been long known.

TABLE XXX

Heats of Formation of

C—hal *in Alkyl Halides*

Halide	Link	H_a
Methyl chloride	C—Cl	74.7
Ethyl chloride	C—Cl	77.6
Propyl chloride	C—Cl	79.3
Isobutyl chloride	C—Cl	81.5
Methyl bromide	C—Br	61.5
Ethyl bromide	C—Br	64.3
Propyl bromide	C—Br	66.8
Methyl iodide	C—I	44.3
Ethyl iodide	C—I	46.6

C—O *in Alcohols*

Alcohol	Link	H_a
Methyl	C—O	75.9
Ethyl	C—O	76.8
n-Propyl	C—O	79.2
n-Butyl	C—O	80.1
Isobutyl	C—O	81.0
Amyl	C—O	83.1

The amount of the fall—or rise in the heat of formation—is about 1 to 2 kgm-cal per carbon atom added. Various explanations may be given of this, but none of them is quite satisfactory:

(1) The fall might be due to experimental error, an increasing proportion of the heavier molecules escaping combustion in the calorimeter. To get an idea of the quantities, suppose we have a molecule containing 8 carbon atoms. Its heat of combustion will be of the order of 1000 kgm-cal. The observed fall for 8 carbon atoms will be some 10 to 15 kgm-cal. We must, therefore, suppose that about one per cent, or rather more, escapes combustion. This seems improbable. If this source of error were serious it should vary considerably with the method of combustion, and exact agreement would be impossible. Now the primary standard in the determination of heats of combustion is benzoic acid, and other subsidiary standards are salicylic acid, naphthalene and cane sugar, substances containing 7, 7, 10, and 12 carbon atoms respectively in the molecule. The ratio of the heats of combustion of benzoic acid and of naphthalene is given as 1.5201.[25] It is certainly known to 1 part in 1000, and probably to 2 or 3 parts in 10,000. It is difficult to believe that so close an agreement could be obtained by different experimenters if in all cases one or two per cent of the substance remained unburnt. It is also difficult to see why there should be this difficulty with alcohols, acids and esters, but not with hydrocarbons.[26]

(2) If this difference is not due to errors in determining the heats of combustion, it might be due to some systematic error in the calculations. As we have seen, the difference is shown by the heats of combustion themselves and is independent of any assumption as to the heats of atomization of the elements. The only corrections made to the observed heats are for the latent heat of evaporation (and, if necessary, of fusion), and the corrections of these for temperature. The heats of evaporation are obtained: (a) by direct observation; (b) from the variation of the vapor pressure with temperature—Clausius-Clapeyron equation; and (c) by means of Von Wartenberg's equation. Wherever these three methods can be compared their results show a good agreement, and certainly no signs of

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[25] P. Schläpfer and W. Fioroni, *Helv. Chim. Acta*, **6**, 713 (1923). See also P. E. Verkade and J. Coops, *Rec. trav. chem.*, **42**, 205 (1923); *Z. physik. Chem.*, **118**, 123 (1925); W. Swietoslawski, *J. chim. phys.*, **22**, 583 (1925).

[26] With some types of compounds, such as certain acetylene derivatives, incomplete combustion may occur. See P. Landrieu and F. Baylocq, *Bull. soc. chim.*, [4] **45**, 217 (1929).

systematic error. The differences we are seeking to explain are of the order of 1 to 2 kgm-cal for the addition of one carbon atom, that is for a rise of boiling point of about 30 degrees on the average. The whole effect of this rise in boiling point is only to increase the latent heat of evaporation by about 0.6 kgm-cal, so that an error in allowing for it is quite inadequate to explain the change.

In the same way we have assumed a temperature coefficient of the latent heat of evaporation of 0.013 kgm-cal per degree. To account for a difference of 1 to 2 kgm-cal on a rise of 30 degrees we should need a temperature coefficient of 0.03 to 0.06; and as may be seen from the list on page 104, not even sulphur dioxide in the neighborhood of its critical point, gives a value larger than 0.023.

(3) It would seem, therefore, that the difference must be real. If so it might be attributed to our having determined the values at 20° whereas they should, strictly, be determined for molecules that have no rotational or vibrational quanta, that is at the absolute zero. We might imagine that the effect of the increased number of degrees of freedom in the larger molecules would be to enable them to acquire more energy in these forms in rising to 293°Abs. This, however, could only be a second-order effect; in making an allowance for one C—C and two C—H links derived from the heats of formation of methane and ethane we have already assumed a heat content at 20°C proportional to the number of atoms in the molecule, and any further change in ascending the series could occur only if the heat content increased more rapidly than the number of atoms. This explanation also can be shown to be inadequate. The total integrated heat capacity of a gram-molecule from absolute zero to 300°Abs. may be taken to be somewhere between 1 and 2 kgm-cal per atom, and the increase for a CH_2 group therefore from 3 to 6 kgm-cal. It is not likely that the second-order variations of this quantity amount to something like a third of its total amount, as we should require to assume if this hypothesis were adopted.

We are, therefore, reduced to the last explanation: that the heat of formation of the link C—X in $C_nH_{2n+1}X$ is really greater the larger the value of n. This does not seem to be impossible. When a hydrogen atom in a paraffin is replaced by another atom or group X, the equilibrium of the molecule is certainly disturbed. We know that a dipole is formed, and we may suppose that the orbits of the electrons surrounding the carbon atom which carries the group X are to some extent distorted. If there is only one carbon atom in the molecule this has to bear the whole of the distortion, but if there are several it can, at least to some extent, be shared between them. In this way it may happen that the potential energy of the molecule falls, and its heat of formation increases, as the molecule becomes larger. This view is supported by the observation that no such effect occurs with the paraffins, *i.e.* where X = H. Here there will be no distortion of this kind, and so the values of the heats of formation of the links should be independent of the number of atoms in the molecule, as in fact they are found to be. But though we can understand why this rise might not be observed with the hydrocarbons, it is difficult to explain its occurrence in practically all other types of organic compounds, and to about the same extent irrespective of the nature of the groups that they contain.

This suggestion is not offered as a final solution of the problem; but it is necessary to mention the difficulty and deal with it as best we can. For a more detailed discussion we should require to determine the magnitude of the increase per carbon atom, and its relation to the nature of the group X. This is very difficult to do. The increase per carbon atom is of the same order as the errors in the measurement of an individual heat of combustion. If we plot for a series of homologues the values of the calculated heat of formation of a particular link against the number of carbon atoms in the molecule, while we cannot fail to recognize the general tendency of the values to rise, it is impossible to give more than a very rough estimate of the slope of the curve. The obvious suggestion of examining the highest members of the series, is impracticable because it is precisely these compounds for which the errors in the heats of combustion produce the largest effects on the calculated value of the heat of formation of a unique link in the molecule, and also for which the uncertain correction for the latent heat of evaporation at 20° is the largest.

All that we can do at present is to note this variation and, where the heats of combustion are at all uncertain, to plot the values for a series of homologues, to draw the most probable curve relating the value for the link to the number of carbon atoms, and, in order to reduce the values to a common basis, to give that which corresponds to the lowest carbon content. This has been done for all the values quoted in Table XXXI.

Most of the data in Table XXXI are straightforward; but for those having reference letters assumptions have been made that are discussed in the corresponding notes.

TABLE XXXI

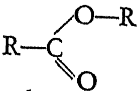
Heats of Formation of Links

(In kgm-calories)

Link	Heat	Substances	Link	Heat	Substances
H—H	103.0	H_2 gas	N≡N	208	N_2 gas
C—C	75	Diamond	N—H	89.8	Ammonia[c]
C_{al}—C_{al}	71.14	Paraffins	N—H	87.0	Alkylamines[c]
C_{al}—C_{ar}	79·40	Aromatic	O═O	118	O_2 gas
C_{ar}—C_{ar}	97·17	Aromatic	O—H	110.0	H_2O gas[d]
C═C	123	Olefines	O—H	106	Alcohols[d]
C≡C	161	Acetylenes	S═S	104	S_2 gas
C_{al}—H	93·61	Paraffins	S—H	88.2	H_2S[e]
C_{ar}—H	101.73	Aromatic	S—H	85.0	Mercaptans[e]
C—N	60.0	Alkylamines[a]	Se—H	ca. 66	H_2Se
C═N	125.3	Isocyanates[a]	Te—H	ca. 54	H_2Te
C≡N	183.0	Cyanogen	F—F	64.0	F_2
C≡N	187.5	Acetonitrile	Cl—Cl	57·4	Cl_2
C≡N	183	Isocyanides	Br—Br	49.8	Br_2 gas
C—O	76.5	Ethers	I—I	36.0	I_2 gas
C—O	79·5	Acetals	F—H	147.6	HF
C═O	160	Aldehydes	Cl—H	102.2	HCl
C═O	167	Ketones	Br—H	86.7	HBr
C═O	182	Esters[b]	I—H	70.9	HI
C═O	181.3	Carbon dioxide	N—F	75·3	NF_3
C≡O	235·5	Carbon monoxide	N—Cl	59	Cl—N═O[g]
C—S	62	Alkyl sulphides	N—O	64.2	Methyl nitrite[f]
C—S	59·3	Thiocyanates	N═O	125	Nitrous oxide[g]
C═S	128.6	Carbon bisulphide	Cl—O	47.2	Cl_2O
C═S	130.9	Isothiocyanates	Cl—F	88.1	ClF
C—Cl	75	Alkyl chlorides	Cl—Br	52.8	ClBr
C—Br	62	Alkyl bromides	Cl—I	47·6	ICl
C—I	45	Alkyl iodides	Br—I	42	IBr

NOTES TO TABLE XXXI

[a] C═N, this is on the assumption that in R—N═C═O the C═O link has the same value (167) as in the ketones.

[b] C═O, 182 kgm-cal in esters. It is here assumed that in  $R{-}C({-}O{-}R){=}O$ the C—O—R links have the same heat of formation as in the ethers. We should expect to find that the carbonyl group had a larger energy-content in the esters than in the aldehydes and ketones, since it is less reactive; but the difference is unexpectedly great, and it is remarkable that the same difference should be shown by the C═O group in carbon dioxide.

[c] N—H, 87 in alkylamines, 89.8 in ammonia.

[d] O—H, 106 in alcohols, 110 in water.

[e] S—H, 85.0 in mercaptans, 88.2 in hydrogen sulphide.
The N—H value in the alkylamines is got by a comparison of the primary, secondary and tertiary amines, which gives us independent values for C—N and N—H. The O—H and the S—H values are obtained by assuming that C—O and C—S are the same in the alcohols and mercaptans as in the ethers and thioethers respectively. It will be noticed that the heats of formation of all three links, N—H, O—H and S—H are 3 or 4 kgm-cal less in the organic compounds than in the hydrides. This may be due to the greater symmetry of the latter.

[g] N═O, 125 kgm-cal is half the heat of dissociation of nitrous oxide, of which the formula may be taken to be $N \overset{\leftarrow}{=} O \overset{\rightarrow}{=} N$.

[f] N—O, 64.2; this is obtained from the heat of formation of methyl nitrite, $CH_3{-}O{-}N{=}O$, using the value 125 for N═O.

EFFECT OF MULTIPLE LINKS

The change with the multiplicity of the link of the heat of combination of carbon with carbon has already been discussed. Table XXXII gives the mean absolute and relative heats of single, double, and triple links for all the elements for which we have data.

TABLE XXXII

Heats of Formation of Multiple Links

Link	Absolute			Relative		
	$A{-}B$	$A{=}B$	$A{\equiv}B$	$A{-}B$	$A{=}B$	$A{\equiv}B$
C—C	71	123	161	1	1.73	2.26
C—N	60	125	184	1	2.08	3.07
C—O	77	164	235.5	1	2.13	3.06
C—S	62	129	—	1	2.08	—
N—O	64	125	—	1	1.95	—

The exceptional position of the C—C link is very marked. A possible reason is that in all the links except this, at least one of the atoms concerned has unshared valence electrons, which may be capable of taking up the strain.

Chlorination Products of Methane

In methylene chloride, chloroform, and carbon tetrachloride we know the magnitudes of the valence angles (page 89); and it is of interest to see what are the heats of formation. The values for one C—Cl link in compounds of this class are given in Table XXXIII.

TABLE XXXIII

Heats of Formation for a C—Cl Link in the Chlorination Products of Methane

CH_3Cl	C—Cl	74·7 kgm-cal
$CH_3{\cdot}CH_2Cl$	C—Cl	77·6
$CH_2Cl{\cdot}CH_2Cl$	C—Cl	75·9
$CH_3{\cdot}CHCl_2$	C—Cl	75·8
$CHCl_3$	C—Cl	72·5
CCl_4	C—Cl	72·6

The differences are small; but there is an indication that as the number of chlorine atoms attached to one carbon atom increases and these are pressed closer together, the heat of formation diminishes and the energy-content of the molecule increases.

FORCE CONSTANTS OF LINKS

A characteristic property of a covalent link that may be discussed here, since it is an energy property, is the force constant already mentioned in connection with the spectroscopic methods of determining interatomic distances (see page 72). This constant measures the resistance of the link to deformation. Its importance was first pointed out by Dadieu and Kohlrausch,[27] who were able to identify particular lines in the Raman spectra of organic compounds with particular atomic groups. The Raman lines, as we have seen, are due to the absorption by the molecule of vibrational quanta, which changes the frequency of the light by an amount ν, and its energy by $h\nu$. This energy change must be equal to the vibrational quantum, which is $h\omega$ where ω is the frequency (sec^{-1}) of the vibration. We can thus determine the magnitude of the restoring force K which resists the change in the length of the link. For small displacements it may be assumed that the force is proportional to the displacement x, so that

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[27] A. Dadieu and K. W. F. Kohlrausch, *Ber.*, 63, 251, 1675 (1930); Kohlrausch, *Der Smekal-Raman Effekt* (Berlin, 1931), p. 154.

$$K = f.x$$

where f is the force constant. For a simple diatomic system of this kind it follows from elementary mechanics that:

$$\omega \text{ (dynes/cm)} = \frac{1}{2\pi}\sqrt{\frac{f}{M}}$$

where M is the "reduced mass" given by

$$1/M = 1/M_1 + 1/M_2,$$

M_1 and M_2 being the masses of the atoms.

Thus if we know the displacement of the Raman lines, and the atoms that compose the vibrating link, we can calculate the force constant, f. We can also find the amplitude a of the vibration and the mean restoring force K during the vibration, from the equations:

$$a \text{ (cm)} = 8.187 \times 10^{-8} \sqrt{1/M\omega}$$

$$K \text{ (dynes)} = 24.0 \times 10^{-10} \sqrt{M\omega^3}$$

Values of the force constant, f, for a series of single, double and triple links, are given in Table XXXIV; they are taken from the works of Dadieu and of Kohlrausch already quoted.[27] They are roughly proportional to the heats of rupture of the links to which they refer; in fact it has been shown that the ratio $f:A$ varies over a wide range of examples only in the proportion of about 2:1.

It is interesting to compare the variation of the force constant, and its dependence on the multiplicity of the link, with the behavior of the heats of formation given in Tables XV and XXXI. The results of this comparison are given in Table XXXV.

TABLE XXXIV

Force Constants from Optical Data

(f in dynes/cm × 10^5)

Single Links

Link	f	Compound	Link	f	Compound
H—H	5.06	H_2	C—C	4.31	C_2H_6
Cl—Cl	3.21	Cl_2	C—Cl	3.12	CH_3Cl
Br—Br	2.47	Br_2	C—Br	2.61	CH_3Br
I—I	1.69	I_2	C—I	2.15	CH_3I
H—Cl	4.4	HCl	C—S	3.01	CH_3SH
H—Br	3.56	HBr	S—H	3.77	CH_3SH
H—I	2.9	HI	C—N	4.86	CH_3NH_2
S—O	4.93	SO_2	N—H	6.04	CH_3NH_2
N—H	6.39	NH_3	C—O	4.99	CH_3OH
C—H	4.58	CH_4	O—H	6.34	CH_3OH

Double Links

Link	f	Compound
O=O	11.3	O_2
S=O	7.23	SO_2
C=C	9.36	C_2H_4
C=O	11.9	H_2CO

Triple Links

Link	f	Compound
N≡N	22.2	N_2
C≡O	18.6	CO
C≡N	17.9	HCN
C≡N	17.9	CH_3CN
C≡C	16.4	C_2H_2

TABLE XXXV

Comparisons of Force Constant and Heat of Formation

		Force constant	Heat of formation
Single links:	Maximum	6.39	148
	Minimum	1.69	36
	Ratio	3.8	4.1
	Mean	4.02	75
Double links:	Maximum	11.9	182
	Minimum	7.23	104
	Ratio	1.6	1.8
	Mean	9.95	134
	Mean per link	5.0	67
Triple links:	Maximum	22.2	236
	Minimum	16.4	161
	Ratio	1.4	1.5
	Mean	18.6	197
	Mean per link	6.2	66

It will be seen that the variations, and the influence of the multiplicity, are much the same for both constants; the greater variability of the single-link values is largely due to our having far more data for this class of link.

The heats of formation are of more importance inasmuch as they tell us the thermodynamic stability of the molecule; but the force constants have the advantage that it is possible, with the help of the Raman data, to follow the variation of the constant for a particular link through a whole series of molecules, and find how it is affected by the other groups that the molecule contains. The investigation of this subject has only recently begun, and at present it has scarcely got beyond the qualitative stage. There is no doubt, however, that it will prove of great value, because it enables us to observe the behavior of one particular link in a number of molecules, whereas with such properties as the heat of formation and the electrical dipole moment we can measure only the value for the whole molecule, and the elimination of the contributions to this value made by the other links in the molecule always involves some uncertainty.

CHAPTER V

ELECTRICAL DIPOLE MOMENTS

Literature of Dipole Moments

This subject, which is, for practical purposes, scarcely more than four years old, has already attained great importance, and the literature is considerable. In addition to papers in journals, which will be referred to in due course, there are a series of monographs of which the most important and authoritative is Debye's *Polar Molecules*;[1] its German edition, published later in the same year, contains more material, and two supplementary lists have been issued, with all the moments measured up to the end of 1929 and 1930 respectively. This work goes far more deeply into the underlying questions of pure physics than I have attempted to do. Höjendahl's dissertation[2] gives a useful review of the subject, with discussions of many of the more important questions. Sack's article[3] I have found most valuable. The volume of *Leipziger Vorträge* for 1929 contains a series of original contributions of importance. Williams has published a useful discussion under the title "Molekulare Dipolmomente und ihre Bedeutung für die chemische Forschung."[4]

Smyth's recent volume[5] gives a full discussion of the theory of dipole moments and the chemical bearing of the results, and further of certain allied subjects, such as the refractive power. It also contains a list of the most probable values of the moments of all substances that have been measured up to the spring of 1931. It is unfortunate that neither Debye's nor Smyth's list states the conditions of measurement, whether the substance was a gas or in solution, and if the latter, in what solvent; nor do they state whether the electron polarization was eliminated by the optical or the temperature method.

I would also acknowledge my indebtedness to Dr. L. E. Sutton of Magdalen College, Oxford, for many valuable suggestions and criticisms on this chapter.

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[1] Debye, *Polar Molecules*, Chemical Catalog Co., New York, 1929. 172 p. (German edition: *Polare Molekeln*, Leipzig, 1929).

[2] Höjendahl, *Studies of Dipole Moments* (Dissertation, Copenhagen, 1928; in English).

[3] Sack, "Dipolmoment und Molekularstruktur," *Ergebnisse exakten Wissen.*, 8, 307–366 (1929).

[4] J. W. Williams, *Fortschritte Chem., Physik, physik. Chem.*, 20, Heft 5 (1930).

[5] C. P. Smyth, *Dielectric Constant and Molecular Structure*. New York, 1931. 214 p. (Am. Chem. Soc. Monograph Series, No. 55).

EVERY molecule consists of positive nuclei surrounded by negative electrons. If their arrangement is such that the center of action of the positive parts coincides with that of the negative parts, the molecule is non-polar and has no tendency to take up any definite position in an electric field. If the two centers do not coincide, the molecule is polar:[6] it is equivalent electrically to a rod with a negative charge at one end and a positive charge at the other, and in the field will tend to arrange itself with its negative end toward the positive pole. It is thus said to possess an electrical dipole moment, the magnitude of which is given by the product of the charge, e, on one end of the equivalent rod, into the distance, d, separating the two charges.

Every isolated atom is non-polar. When two neutral atoms form a covalent link, and share two electrons between them, they may or may not acquire a dipole moment. If the two electrons are shared equally, so that they count as much for each of the atoms, the center of action of the negative parts will not be altered and the molecule will have no moment. But if they are shared unequally, the molecule will be polar, the atom which has the larger share of the two binding electrons being the negative end of the dipole.

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[6] This is the original meaning of the words "polar" and "non-polar" in physics, and it is very desirable that chemists should not use them in any other. Their employment in chemistry with a quite different sense originated in a paper by G. N. Lewis—*J. Am. Chem. Soc.*, 35, 1448 (1913)—in which he distinguished two forms of chemical combination differing "not only in degree but also in kind": a polar form, as in potassium chloride, and a non-polar, as in methane. Lewis gave lists of typical polar and non-polar substances; his polar list includes not only definite salts, but also associated substances such as alcohol; his non-polar list contains covalent non-associated substances such as the hydrocarbons. This has led to the use of the terms polar and non-polar to distinguish abnormal associated liquids from normal and non-associated—cf. Hildebrand, *Solubility* (New York, 1924), p. 84. Other chemists use the words to designate electrovalent and covalent molecules. In this way a double confusion has arisen. In the first place, Lewis' list of polar substances includes both electrovalent compounds, like potassium chloride, and covalent compounds, like the alcohols and water. Secondly, his non-polar liquids, although they are all covalent, are some of them non-polar in the proper sense, such as the paraffins and benzene, while others are definitely polar such as toluene or chloroform. The meaning of the terms as now used is thus entirely ambiguous. Everyone would call potassium chloride polar, and methane non-polar. Alcohol would be called polar by Lewis and Hildebrand and by the physicists, but not by those who use "polar" as meaning "electrovalent." Chloroform (or toluene) would be called non-polar by Lewis and Hildebrand and by those who use the word in the sense of covalent, but polar by the physicists, since it has a definite dipole moment.

The only way out of this confusion is to avoid using the words "polar" and "non-polar," except in their original physical sense of possessing or not possessing an electrical dipole moment. The two kinds of linkage can be called "electrovalent" and "covalent"; the two kinds of liquids, whose differences Hildebrand discusses, can be distinguished as "abnormal" and "normal."

In Lewis' original formulation of the covalent link, the question of the equality or otherwise of the sharing was not discussed; indeed on the static model that he used this question did not arise. It thus came to be assumed that the sharing was equal, and that normal covalences gave rise to non-polar molecules.[7] The physicists, however, had shown before this that certain molecules, such as water and hydrochloric acid, must be polar. Debye pointed out[8] that this must be assumed in order to explain the change of polarizability with temperature, and he deduced the formula relating these two magnitudes. Two years later J. J. Thomson[9] did the same thing, and he subsequently developed the idea,[10] showing how polar and non-polar molecules could be distinguished experimentally by the fact that the former did not agree with Maxwell's law that the dielectric constant was equal to the square of the refractive index (below, p. 128). The methods by which the magnitudes of these moments can be measured are mainly due to Debye, who has developed and simplified them greatly during the last few years. We now realize that the dipole moment is one of the most fundamental characteristics of the covalent link, and has an important relation to its behavior.

METHODS OF MEASUREMENT

The methods employed for measuring dipole moments depend almost wholly on the determination of the dielectric constant.[11] If a condenser containing two charged plates *in vacuo* is filled with a dielectric, the potential of the plates falls—the capacity increases—and the attraction between them is diminished. This is due to an influence exerted by the field on the molecules of the dielectric, and the change is a measure of the amount of the influence. The dielectric constant, ϵ, is: (1) the ratio of the capacity of the condenser filled with the medium to its capacity when vacuous. This is identical with (2) the ratio of the electrical force between two charged bodies *in vacuo* to the force between the same bodies in the medium. It can also be shown (3: Maxwell's law) that ϵ is equal to the ratio of the square of the velocity of electromagnetic waves in the medium to the square of their velocity *in vacuo*, or in other words that ϵ is the square of the refractive index, provided waves of the same frequency are used to measure both the dielectric constant and the refractive index.[12] The so-called "Clausius-Mosotti law,"[13] which is true only under certain strict limitations to be considered later, states that the molecular polarization P of a substance of molecular weight M and density d, is related to the dielectric constant by the equation:

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[7] That a co-ordinate link, in which both the linking electrons come from the same atom, must have definite polarity, was pointed out by Lowry and others.

[8] Debye, *Physik. Z.*, 13, 97 (1912).

[9] J. J. Thomson, *Phil. Mag.*, [6] 28, 757 (1914).

[10] J. J. Thomson, *The Electron in Chemistry* (Chapman and Hall, London, 1923), p. 44.

[11] For the conditions of accurate determination of the dielectric constant see N. Hartshorn and D. A. Oliver, *Proc. Roy. Soc. London*, 123, 664 (1929). With benzene they claim to have reached an accuracy of 1 in 10,000.

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$$

This corresponds to the Lorentz-Lorenz formula[14] for the molecular refractive power of a medium of refractive index n:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

which was in fact derived from it and is much more widely applicable, as will be shown later.

If we have a mixture of two liquids of molecular polarizations P_1 and P_2, molecular weights M_1 and M_2, present in the molecular fractions f_1 and f_2 ($f_1 + f_2 = 1$), we can express the mean molecular polarization of the mixture $P_{1,2}$ by writing the Clausius-Mosotti relation in the form:

$$\begin{aligned} P_{1,2} &= \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{f_1M_1 + f_2M_2}{d}\right) \\ &= \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{f_1M_1}{d} + \frac{f_2M_2}{d}\right) \\ &= f_1P_1 + f_2P_2 \end{aligned}$$

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[12] For static measurement of the dielectric constant the value obtained is the square of the refractive index for infinite wave length.

[13] O. F. Mosotti, *Mem. accad. sci. Modena, math.-fis.*, 24, II, 49 (1850); R. Clausius, *Mechanische Wärmetheorie* (Braunschweig, 1879), Vol. 2, p. 62.

[14] H. A. Lorentz, *Ann. Physik*, 9, 641 (1880); L. Lorenz, *ibidem*, 11, 70 (1880).

In this way we can determine the molecular polarization of a substance either alone or as the constituent of a mixture. This is of the dimensions of a volume, and may lie anywhere between 1 and 1000 cc.

If the Clausius-Mosotti formula were strictly true, the value of P obtained for a given substance would be independent both of the concentration and of the temperature. In practice, however, it is found that the value is usually affected by both of these variables. The change with concentration is due to the influence of the dipoles on one another, which naturally increases as they get nearer. It has not yet been found possible to calculate the magnitude of this influence (see below, page 170), and so all that can be done is to eliminate it by removing the dipoles sufficiently far from one another, either by examining the substance as a vapor or by taking a dilute solution of it in a non-polar solvent. In what follows it will be assumed that the concentration of the substance is small enough for the mutual influence of the dipoles to be negligible.[15]

In order to understand the effect of temperature, we must consider the nature of the polarization in more detail. The polarization of the molecules in an electric field can take place in three ways:

(1) The arrangement of the electrons will be displaced with respect to the nuclei towards the positive pole of the field. This is what is called the electron polarization, P_E.

(2) As a result of this deformation of the electronic orbits, the nuclei themselves will be to some extent displaced with respect to one another; this gives the atomic polarization, P_A. This effect is usually small compared with P_E.

(3) These two effects give the molecule a temporary dipole moment, whose direction is determined by that of the field. But if the molecule has a permanent dipole moment of its own—if it is polar—the field will tend to orient it along the direction of the lines of force, giving rise to the orientation polarization, P_O. This tendency will

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[15] This mutual influence makes any conclusions drawn from the dielectric constants of pure polar liquids of little value, except as showing in well-marked instances that they are polar.

be opposed by the thermal agitation or Brownian movement of the molecules. With any fields ordinarily used the amount of orientation is small, and therefore proportional to the field strength, which explains why the dielectric constant is found to be independent of the strength of the field. For very large fields, in which the amount of orientation was very great—approaching "saturation"—this would no longer be true.

Since the orientation—and hence this term of the polarization—is the result of a conflict between the influence of the field and that of the thermal agitation, it must diminish as the temperature increases. The exact relation was deduced by Debye.[8] If we call the electronic and atomic susceptibilities, which are independent of the temperature, α_0 per molecule, the total molecular polarization is given by:

$$P = \frac{4\pi}{3}\cdot N\left(\alpha_0 + \frac{\mu^2}{3kT}\right)$$

where N is the Avogadro number (number of molecules in a gram-molecule $= 6.06 \times 10^{23}$), T the temperature, and k the gas constant per molecule ($k = \mathrm{R}/N$) and μ the dipole moment.

It is thus evident that if we measure ϵ, and hence P, at a series of temperatures, two results are possible. If the molecules are non-polar, and their polarization is only electronic and atomic, we shall find P to be constant. If, however, they are polar, the effect of the last term will diminish as the temperature rises, and the polarization will fall off. The simplest way of calculating the dipole moment is to plot the polarization against the reciprocal of the temperature. Debye's equation is of the form:

$$P = A + \frac{B}{T}$$

where

$$B = \frac{4\pi}{9}\cdot\frac{N}{k}\cdot\mu^2$$

Hence the plot will in any case give a straight line. If the substance is non-polar, $\mu = 0$ and $B = 0$, so that the line is horizontal. If it is polar, μ and hence B have finite positive values, and the line will be inclined to the horizontal at an angle from which μ can be calculated. If we put the numerical values of N and k (1.37×10^{-13}) into the above equation for B, we get:

$$\mu = 0.0127\sqrt{B} \times 10^{-18}$$

in electrostatic units. Thus for ammonia Jona[16] found $B = 15\,250$ cc, whence $\mu = 1.57 \times 10^{-18}$ electrostatic unit. All the dipole moments that have been measured are of this order of magnitude, as is to be expected, since the moment has the dimensions of a charge multiplied by a distance; the electronic charge is 4.77×10^{-10} electrostatic unit, and the molecular distances are of the order of 10^{-8} centimeter.

This method of measuring dipole moments, in which the electronic and the atomic polarizations are eliminated by making determinations at different temperatures, is undoubtedly the most accurate. It can be applied both to gases[17] and to dilute solutions in non-polar solvents.[18] It has, however, the disadvantage that the range of temperature required for accurate results is rather large. With stable gases this may not matter, but with many organic substances the temperature range of stability is somewhat limited.

A more convenient method has been introduced by Debye and Lange that is accurate enough for ordinary purposes, in which the electronic polarization is eliminated in another way.

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[16] M. Jona, *Physik. Z.*, 20, 14 (1919).

[17] For an example of its application to gases see Sänger, *Leipziger Vorträge*, 1929, 1. A peculiar difficulty arises with gases in the determination of the concentration. This is usually calculated from the pressure, assuming the simple gas laws to hold. But the normal departures of gases from these laws are often sufficient, at pressures near that of the atmosphere, to lead to serious errors; these can only be avoided either by actual measurement of the concentration or by measuring the dielectric constant at a series of diminishing pressures, until a point is reached below which the molecular polarization, calculated on the basis of the simple gas laws, is independent of the pressure.

[18] When a substance is believed to be non-polar this can be tested by measuring the dielectric constant of the pure liquid over a considerable range of temperature. Thus Smyth and Stoops—*J. Am. Chem. Soc.*, 50, 1883 (1928)—found that with the isomeric heptanes the molecular polarization varied less than 2 per cent over a range of 200 degrees, and agreed with the refractive power within 1 cc. This is conclusive proof that the substances are non-polar. See also Dornte and Smyth, *J. Am. Chem. Soc.*, 52, 3546 (1930).

If we plot the polarization or refractive power of a polar substance against the wave length of the radiations, over a range from long radio waves down to the ultra-violet, there is obtained a curve of the form shown in Figure 6.

The extent of the electronic, atomic and orientation polarizations are indicated on the vertical axis. The electronic polarization, P_E, is effected by the field with very great rapidity. The electrons have so small an inertia that the distortion of their orbits keeps step with the oscillations of the electromagnetic waves up to very high frequencies lying far in the ultra-violet, say 1000Å and frequency 3×10^{15} waves per second. The atomic polarization, P_A, is much less rapid, owing to the greater mass of the nuclei; it follows the oscillations of the field up to the infrared, say 30 to 300μ and frequency 10^{13} to 10^{12} waves per second;[19] but its effect is small compared with P_E and often may be neglected.[20]

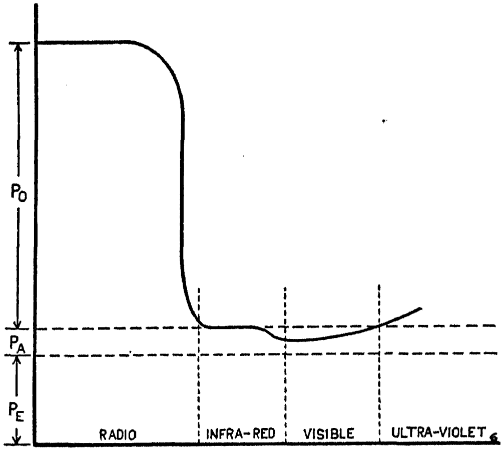

FIG. 6

The third term, P_O, is due to the orientation of the molecules that have permanent dipoles, and this is a relatively slow process requiring about 10^{-10} second, corresponding to very short wireless waves of 3 centimeters.[21] In practice the waves used for measuring dielectric constants are never shorter than 2 meters, partly in order to avoid this region of anomalous dispersion and partly on account of the difficulties of measurement.

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[19] See Ebert, [illegible] 1929, 55.

[20] Wolf—*Physik. Z.*, 31, 227 (1930)—considers that P_A may be taken to be 15 per cent of P_E; but while this probably gives a correct idea of the order of magnitude, it is clear that the actual values vary greatly with different substances.

Accordingly, if we measure the dielectric constant for waves somewhere in the visible spectrum, this will give us the electronic polarization, since there will not be time between one wave and the next for the molecules to turn round. But as we have seen, the dielectric constant for visible light can be obtained from the refractive index by means of the Lorentz-Lorenz formula, which is the Clausius-Mosotti formula with the square of the refractive index in place of the dielectric constant. Thus the electronic and, approximately, the atomic polarization is given by:

$$P_E + P_A = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$$

The value calculated in this way, is subtracted from the total polarization (as measured by means of wireless waves having a wavelength of, say 100 meters and a frequency of 3×10^6) as follows:

$$P_E + P_A + P_O = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{d}$$

and in this way we arrive at the molecular polarization, and so at the dipole moment.

This method of correction is less certain than that which depends on the temperature, especially in two cases: (1) where the electronic and the atomic polarizations are not much less than the total polarization, particularly when it is a question of determining whether a substance has a small permanent moment or none; and (2) if there is an absorption band, due to a quantum effect, near the wavelength selected, since in the neighborhood of such a band the refractive index varies anomalously. The method is thus less certain with strongly colored substances. However, where the results seem, for either of these reasons, to be open to doubt, they can usually be checked by the temperature method.

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[21] See Lunt and Rau, *Proc. Roy. Soc. London*, 126, 213 (1930).

Debye's method then is as follows: The dielectric constants of dilute solutions of the substance to be examined in a non-polar solvent, such as benzene or carbon disulphide, are measured by a wireless method. The molecular polarizations for the solute, P_{total}, are plotted against the concentrations, and the curve extrapolated to infinite dilution, where the mutual influence of the dipoles is zero; this does not usually involve any serious error. The refractive indices are measured, usually with yellow light (sodium or helium) and the calculated molecular refractive powers—unless they are found to be constant—are also extrapolated to infinite dilution. From the extrapolated values the molecular polarization and hence the dipole moment can be determined. The method can thus be used for any substance that is even sparingly soluble in a non-polar liquid, such as benzene or heptane.

This method has repeatedly been checked by comparing its results with those obtained by the temperature method either in the gaseous state or in solution. The agreement, when the moment is not too small, is good.[22] This is illustrated by the following examples, in which the solvent used—if any—is specified under "Method"; T is the temperature method, R is the refractive index method, and as throughout this volume μ is in terms of the unit 1×10^{-18} E.S.U.:

Substance	μ	Method
Acetone	2.84	Gas, T
	2.72	Benzene, R
	2.70	CCl_4, R
Methylene chloride	1.59	Gas, T
	1.55	Benzene, R
	1.48	CCl_4, T
Chloroform	1.05	Gas, T
	1.05	Hexane, R
	1.10	Benzene, R
Quinol diethyl ether	1.76	Benzene, R
	1.72	CCl_4, R
	1.74	CS_2, R
	1.74	Cyclohexane, R

[22] Any value less than 0.4×10^{-18} obtained by the optical method may mean that the substance is non-polar.

It is desirable, however, that wherever the moments are small or of special interest they should be tested by the temperature method. The solvent, when there is one, is also of importance. Those most commonly employed are carbon tetrachloride, carbon bisulphide, paraffins, and most frequently benzene; recent work has shown that benzene in particular is liable to enter into some kind of combination with certain solutes and so affect their moments: thus iodine has a moment of 1.0 in benzene and zero in hexane and cyclohexane;[23] aluminum bromide, which is non-polar in carbon bisulphide, has in benzene a moment of no less than 4.89.[24] When a substance is very slightly soluble in the usual non-polar solvents it is natural to look for one in which it dissolves more freely; but this is dangerous because the very fact of its greater solubility in a particular solvent suggests that it combines with this solvent.

The probable errors of the values obtained by either of these methods[25] do not normally exceed 0.1, the actual values lying, as a rule, for polar substances between 0.4 and 4.0. In the more recent determinations the accuracy has been increased.

Molecular Beam Method

There is a third method of determining dipole moments, quite different from the other two, which though it does not at present give such accurate results, can be employed where the others fail; it has certain other advantages as well, especially in being quite independent of dielectric-constant determinations, so that it affords a welcome confirmation of their results and of the truth of the general theory. This is the method of the molecular beam,[26] founded on the famous atomic beam experiments by Stern and Gerlach for the determination of the magnetic moments of atoms. It was first applied to the determination of the electrical dipole moments of molecules by Wrede,[27] who showed in this way that the molecules or ion-pairs of alkaline halides in the vapor state have moments of the order of 10×10^{-18};[28] the method was greatly extended by Estermann,[29] who applied it to organic substances. The substance to be investigated is heated in a minute oven to a temperature at which it has a perceptible but very low vapor pressure. A stream of molecules very far removed from one another, and with the velocity given by their temperature in accordance with the gas laws, issues from this oven through a narrow slit, about 0.01 mm wide, into a high vacuum. By means of a second slit this beam is cut down to a narrow and very thin ribbon of rays. This ribbon is passed through a highly inhomogeneous electric field, one pole being in the form of a knife-edge in the line of the beam and the other a half-cylinder enclosing this. Finally the molecules are received on a brass plate cooled with liquid air, and the trace that they form is observed through a microscope.

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[23] Williams, *Physik. Z.*, 29, 683 (1928); Müller and Sack, *Physik. Z.*, 31, 815 (1930).

[24] Ulich and Nespital, *Z. Elektrochem.*, 37, 559 (1931).

[25] For a discussion of these errors see: Ebert, *Leipziger Vorträge*, 1929, p. 44.

[26] For a full account of this method and its various applications see R. G. S. Fraser, *Molecular Rays*, Cambridge, 1931.

Under these conditions the molecules are too remote to collide with one another. If the field is not on, they go straight through the apparatus and condense in a narrow vertical line on the receiver. If the field is put on—Estermann used 21,000V—it will affect even non-polar molecules; the electronic polarization produces an induced dipole, and this leads to a movement towards the stronger part of the field, so that the trace is shifted; thus with the non-polar diphenyl it was shifted by 0.1 mm. But as the direction of the induced dipoles is wholly determined by that of the field, all the molecules are affected equally, and the trace shifts as a whole, retaining its narrow form, less than 0.15 mm wide. If however the molecules are polar, the displacement caused by the field on any one of them depends on the direction which the dipole has with respect to the field as it passes through; and as these directions are distributed at random[30] the result is to broaden the trace, and the amount of broadening is a measure of the dipole moment. It has not yet been found possible to relate the broadening accurately to the moments; but comparative observations with substances whose dipole moments had been measured by means of the dielectric constant, showed a good qualitative agreement and made it possible to get a rough measure of the moments of other substances. For example, the following breadths of trace were observed:

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[27] Wrede, *Z. Physik*, 44, 261 (1927).

[28] The internuclear distances in these halides being from 2 to 4Å, their moments, if the ions are not distorted, should be from $10 \times$ to 20×10^{-18} electrostatic units.

[29] Estermann, *Z. physik. Chem.*, **B1**, 162 (1928); *ibidem*, **B2**, 287 (1928); *Leipziger Vorträge*, **1929**, p. 17.

diphenyl ($\mu = 0$)	<0.15 mm
diphenyl ether ($\mu = 1.0$)	0.30 mm
methyl *p*-aminobenzoate (μ 3.3)	0.7 mm

No doubt when the technique is further developed the accuracy will be much increased.

This molecular beam method is available for use with substances that cannot be examined by the other methods because they are not soluble enough in non-polar substances, and are not sufficiently volatile at temperatures at which they remain undecomposed to give vapors sufficiently dense for their dielectric constants to be measured. Both these difficulties are likely to arise with compounds of high melting point. The only necessary condition of its application is that the substance should be capable of being sublimed in a high vacuum. The most remarkable instance in which it has been used is that of penterythritol, $C(CH_2OH)_4$, whose melting point is 250° to 255°, which was shown to have a moment of about 2.0. The theoretical bearing of this result is discussed later.

The method has the further advantage that it gives a direct measurement of the behavior of individual molecules so far apart that no possible complications can arise through their interaction with one another or with a solvent.

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[30] The separation into two traces observed in the magnetic experiments of Stern and Gerlach and their followers, does not occur here. The moments of inertia of the molecules are so much greater than those of the atoms in the magnetic experiments that the electric fields employed are not sufficient to bring about the separation. It is possible that with further refinements of experimental detail the separation may be made perceptible.

RESULTS

We have now to consider the results obtained by these various methods. Here there are certain preliminary points to be noticed.

(1) Since the gases are examined at low pressures, and the results in solution are extrapolated to infinite dilution, association in the ordinary sense, as for example with alcohols, is excluded.[31]

(2) The value obtained is in every case that of the resultant moment of the whole molecule, and except in diatomic molecules is made up of several individual moments that must be compounded vectorially, as directed magnitudes. As our object is to discover the moments of individual links, we shall have to consider by what means, and with what accuracy, the separate values can be disentangled.

(3) The value obtained is that of the moment $\mu = e \times d$, but this does not tell us the separate values of e and d for the shared electrons.

(4) The result of the measurement is to give us the magnitude of the moment, but not its direction. Thus the dielectric constants show that the moment of hydrogen chloride is 1.03, but we do not know from this whether the hydrogen or the chlorine is the positive end of the dipole. With some molecules, as with hydrogen chloride itself, this may be more or less certain from other considerations, but very often it is in doubt. A very ingenious method was suggested by J. J. Thomson[32] and worked out by Williams,[23] which is of great aid in settling this question. If two groups are introduced into the *para* position in benzene, they will be symmetrically disposed with respect to the ring, which we now know to be plane; if their moments are similarly directed with respect to the carbon atoms to which they are joined, they will oppose each other and the resultant moment will be approximately the difference of those produced by each group separately; if they are oppositely directed it will be their sum. Strictly

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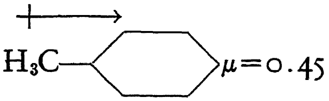
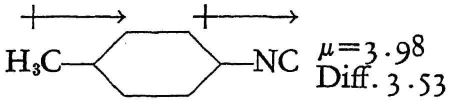
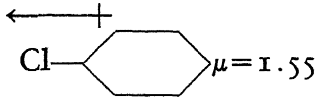
[31] Where the tendency to association is exceptionally strong, as in the carboxylic acids, this is probably no longer true.

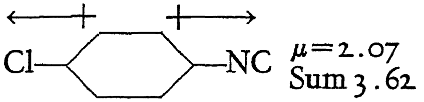
[32] J. J. Thomson, *Phil. Mag.*, [6] 46, 513 (1923).

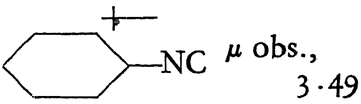
speaking, this does not tell us the direction of the moments; it only enables us to divide the links in question into two classes, C—A and C—B, and to say that the moments of the C—A class are oppositely directed to those of the C—B class. But when we have classified them in this way we have enough other evidence to decide the direction in each class. As an example of the application of this method we may take the isocyanide group,—NC. We have the following values:











It is clear that the moment of the isocyanide group is strengthened by that of a methyl in the *para* position, and weakened by that of a chlorine. Since the moment of the Cl—C link is known to have its negative end, and that of a methyl its positive end, away from the ring, it follows that that of the isocyanide group must have its negative end remote from the ring as the arrows indicate.[33]

We may now proceed to the more important of the experimental results, beginning with the simplest. All molecules in which either there are no polar links,[34] or these are symmetrically arranged so as to balance one another, must be non-polar. Accordingly we find that the inert gases are non-polar,[35] having no links at all; so also are the diatomic elementary gases hydrogen, nitrogen and oxygen, in which, as the atoms are similar, the electrons are presumably equally shared. The small moments recorded for chlorine, 0.23,[36] and bromine, 0.49,[37] are probably erroneous; iodine, as we have seen, is non-polar in solution in hexane and cyclohexane.

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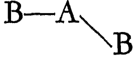
[33] It is natural to regard the moments as due to a shift of the shared electrons from the mean position of zero moment, and to represent the sense of the moment by an arrow pointing in the direction in which this shift may be imagined to take place, *i.e.* towards the negative end of the dipole. This convention is adopted here. Some physicists, however, consider that positive electricity should be regarded on account of its name as having the greater dignity and hence adopt the opposite convention, with the arrow pointing toward the positive end. To avoid confusion, the arrow is here written with a + at its tail so that it may be clear which is the positive end.

[34] This phrase is used in its correct physical sense, as meaning links that possess a dipole moment; all the links with which we are concerned are, of course, covalent. See note above, p. 126.

Diatomic molecules of compounds, such as hydrochloric, hydrobromic and hydriodic acids, and carbon monoxide, are all polar so far as they have been measured.

Triatomic molecules of the type AB_2—the moment of ozone is unknown—should be non-polar if the three atoms lie in a straight line with A in the middle, provided the two links are the same, as they normally will be. If, however, the links form an angle  the molecule will be polar with a moment $M = 2m \cos\frac{1}{2}\theta$, where θ is the angle, and m the moment of a single A—B link.[38] Thus the moments give valuable information as to the stereochemistry of these molecules. The experimental results afford a striking confirmation of the correctness of the tetrahedral model of van't Hoff.[39] Where the link between A and B is single, B—A—B, the molecule is always found to be polar, since the valences are inclined to one another, *e.g.* H_2O, 1.84 and H_2S, 1.0. Where the links are double, B═A═B, the tetrahedral model obviously requires that they shall be in the same straight line, and we find that O═C═O and S═C═S are non-polar; so also is nitrous oxide, which must therefore be supposed to have the structure $\mathrm{N}\overset{\textstyle -}{\leftarrow}\mathrm{O}\overset{\textstyle -}{\rightarrow}\mathrm{N}$. The polarity of sulphur dioxide, 1.7, may be taken to show that the second oxygen atom is attached by a co-ordinate link, O═S→O.

Tetratomic molecules AB_3, with all the A—B links single, will be non-polar if all the four atoms lie in a plane and all the angles between the valences are equal, as in that event they presumably would be. On the tetrahedral model A should lie out of the plane of the three Bs, forming a triangular pyramid, and the molecule should therefore be polar. In agreement with this conclusion we find that ammonia is polar, 1.5, and so also are phosphine, 0.55, arsine, 0.15, and the trihalides of phosphorus, arsenic and antimony.[40]

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[35] Watson, Ras and Ramaswamy, *Proc. Roy. Soc. London*, 132, 569 (1931).

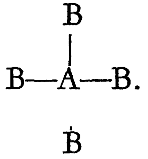
[36] Zakrzewski and Doborzynski, *Bull. acad. polon.*, A, 300 (1930).

[37] Anderson, *Proc. Phys. Soc. London*, 40, 62 (1938); Doborzynski, *Z. Physik*, 66, 657 (1930).

[38] For the tetrahedral angle of 109° 28′, $M = 1.155m$.

[39] For further discussion see Chapter VI, on Stereochemistry (p. 225).

Pentatomic molecules, AB_4, should be non-polar both on the tetrahedral model and also on the plane model,



$$\begin{array}{c} B \\ | \\ B\text{—}A\text{—}B. \\ | \\ B \end{array}$$

Methane, the tetrachlorides of carbon, silicon and titanium, and tin tetraiodide have all been shown to be non-polar; and the plane model is impossible because it requires that methylene chloride, CH_2Cl_2, should be non-polar in the *trans* form, which must be the more stable, whereas it has a moment of 1.5.

These simple examples, in which there is never more than one kind of link in the molecule, illustrate the general principles on which polarity depends. Before we come to the quantitative aspect of the subject we have to consider one particular link, that of hydrogen to carbon, which is of peculiar importance because so much of the evidence about dipole moments is drawn from organic chemistry. All the saturated paraffins that have been examined, whether with straight or with branched chains, have been found to be non-polar. This has been established for 22 different paraffins, including all the normal saturated hydrocarbons up to dodecane and all the nine possible heptanes.[41] It might be supposed that this indicated that the C—H link is non-polar—we may assume this to be true of the other link concerned, C—C. As a fact, however,

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[40]

PCl_3	0.80	$AsCl_3$	1.97	$SbCl_3$	4.06
PBr_3	0.61	$AsBr_3$	1.66		

Bergmann and Engel, *Physik. Z.*, 32, 507 (1931).

[41] Smyth and Stoops, *J. Am. Chem. Soc.*, 50, 1883 (1928); Dornte and Smyth, *ibidem*, 52, 3546 (1930).

it is compatible with any value of the C—H moment. The absence of polarity in methane is explained by its symmetry, independently of the value of the moment of C—H. This implies that the moment of one of the four C—H links must cancel the resultant of those of the other three, and so must be equal and opposite to it. Hence, if in any molecule we replace a $-\!\!\!\!>\!C{-}H$ group by a $-\!\!\!\!>\!C{-}CH_3$ the moment will not be changed—provided, of course, that we can assume the rest of the molecule to be unaffected. But every paraffin can be built up from methane by the successive replacement of hydrogens by methyl groups; and so, whatever may be the moment of the C—H link, the paraffins should all be non-polar, as in fact they are found to be. It should be observed that this argument applies only to the saturated hydrocarbons; the replacement of a hydrogen attached to doubly or aromatically linked carbon by a methyl group is found to alter the moment.

If this argument held universally it would follow that all the homologues of any given organic compound would have the same moment, since the higher may always be obtained from the lower by suitable replacements of hydrogen by methyl. This is found, experimentally, to be nearly but not quite true. Thus the moments of 9 primary alcohols from C_1 to C_{12} vary only from 1.6 to 1.7; secondary and tertiary alcohols give slightly higher values, but scarcely any higher than 1.8. Again, of 10 dialkyl ketones from C_3 to C_{10} the moments all lie between 2.69 and 2.79. The influence of the size of the alkyl group is thus not much larger than the experimental error, and its investigation involves an accurate determination of the moments. Such an investigation has recently been carried out by Sänger,[42] who used the gas-temperature method, and worked at pressures that were shown to be low enough for the simple gas laws to be obeyed (see page 131). He found that methyl and ethyl chlorides showed only a very small difference: CH_3Cl, 1.86 ± 0.03 and C_2H_5Cl, 1.99 ± 0.03—the moments of the monochlorides of the higher alkyls all appear to lie between 1.9 and 2.1—but with the ethers the difference was much larger and the moment definitely fell with an increase in the number of carbon atoms: methyl ether 1.32 ± 0.02, ethyl ether 1.10 ± 0.02, propyl ether 0.85 ±0.03. The occurrence of this fall with the ethers, as contrasted with the relative constancy of the moments in the alkyl halides, alcohols and ketones, is easily explained. The two oxygen valences in the ethers are inclined to each other, as the existence of the moments shows, and presumably in methyl ether at about 109°. As the alkyl group increases in size there will be a tendency, owing to the "flexibility" (see p. 156) of the carbon chain and the effect of the thermal agitation, for this angle to increase in size and any such increase must diminish the dipole moment. No such effect will occur in the alkyl halides, alcohols or ketones.

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[42] Sänger, *Leipziger Vorträge*, 1929, p. 1.

Coming now to the quantitative side of the question, we may consider first the results obtained with diatomic compound molecules, where the conclusions are most certain since there is only one link in the molecule. These however, are very limited in number being confined to the halogen hydrides and carbon monoxide, of which the latter requires special discussion and will be dealt with later (page 187).

With hydrogen chloride, bromide and iodide, since the moments are known, and also, from the band spectra, the distance between the atomic nuclei, we are in a position to discover what the inequality of the "electron sharing" really is. It is obvious that if the molecule were electrovalent and we could disregard any polarization of the electron orbits, its moment would be equal to the electronic charge of 4.77×10^{-15} E.S.U. multiplied by the distance between the two atomic centers; if the two electrons were shared equally the moment would be zero. The imperfection of the sharing is, therefore, the ratio of the observed moment to that which the molecule would have if it were ionized.[43] It may be expressed by calculating from the dipole moment the length of the equivalent dipole, by dividing the moment by the electronic charge, and finding the ratio of this to the actual distance between the nuclei. The figures for the halogen hydrides are as follows:

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[43] This way of regarding the observed moment as due wholly to the pair of shared electrons, though it is convenient, is not strictly correct. The unshared electrons, especially those of the valence group, must play some part; they are polarizable, and must be affected by the field of the dipole, but how much of the effect should be attributed to them we do not know. It still remains true, however, that the observed moment tells us what fraction of the electrostatic disturbance which the transference of an electron would produce is caused by the covalent link.

	$\mu \times 10^{18}$	Dipole length × 10	Distance × 10^8	$\frac{\text{Dipole length}}{\text{Distance}}$
HCl	1.03	0.216	1.27	0.170
HBr	0.78	0.164	1.41	0.116
HI	0.38	0.080	1.61	0.050

It thus appears that in these compounds the inequality of the sharing is from 5 to 17 per cent. That such a result is not peculiar to compounds of hydrogen, as might be suspected, can be shown by making similar calculations for other links, such as that of carbon to chlorine, which gives an inequality of about 20 per cent. These calculations are less certain since they depend on the moments of polyatomic molecules, but they all lead to the same conclusion: that the imperfection of sharing of the electrons in a normal covalence does not much exceed 20 per cent.

Most of the compounds whose dipole moments have been determined are organic substances with more or less complicated molecules; and we can only use these results to calculate the moments of individual links, if we make certain assumptions as to the effect of the rest of the molecule upon them. In any case, the calculation can only be approximate, but the results are not without value, and it is necessary to be quite clear what the preliminary assumptions are, and how far they can be shown experimentally to be justified. The first is that the actual moment of a link is not seriously affected by the other links that its constituent atoms may form; in other words, that the molecular moment—which is what we actually measure—is additively made up of the moments of the separate links which must of course be added as vector and not as scalar quantities. This assumption certainly is not strictly true. As we have already seen, the replacement of a hydrogen atom attached to carbon by a methyl group does not affect the moment of the molecule if the carbon is part of a saturated chain; but it does so if it is doubly linked or part of an aromatic nucleus. In general, it is found that the moment of the link C—X, or, to speak more accurately, the difference between the moments of R—H and R—X, is different according as the carbon is saturated or is aromatic—or according as R is aliphatic or is aromatic—as is to be seen from the list in Table XXXIX (p. 179). Apart from such specific differences, however, the moment of a link seems not to be affected by the other links present in the molecule much beyond the limits of experimental error, which it must be remembered are in dipole moments rather wide. This is in accord with our general conclusions. We have seen that many of the properties of a covalent link, such as the distance between the nuclei and the heat of rupture, are but little affected by the other atoms or groups that are present. We may therefore assume that this is true of the moments, as a first approximation. There can be little doubt that when we are able to measure the moments in the less simple molecules with greater accuracy, we shall find that this mutual influence of links exists, and that it plays an important part in determining the reactivity of the molecule. This is, indeed, the principle that underlies the "electron drift" theories of reactivity of the modern organic chemist, theories the truth of which is already beginning to be tested by the study of dipole moments (see p. 178). But for our present purpose, of getting an approximate idea of the relation of the moment of a link to the nature of the linked atoms, this complication may as a rule be neglected.

A more serious difficulty is met with when we try to determine the resultant of the moments of a series of links in a molecule. To do this we must know not only their magnitudes but the angles between them. As a first approximation, these angles may be assumed to be those required by the tetrahedral model—for example, 109° 28′ in a saturated molecule; but we already have direct evidence from Debye's work on the X-ray scattering of gases (page 89) that considerable departures from these angles occur.

Further uncertainty has been introduced into these calculations by the recent work of Pauling,[44] who has concluded from wave mechanics that, while the normal valence angle with a 4-covalent atom is 109.5°, where the covalence is 2 or 3 the angle is 90°. This would seriously affect the values obtained for single links from the moments of molecules whose central atoms have covalences less than 4. For example, water has a moment of 1.85. If the valence angle is 109.5° then m(O—H)[45] is $1.85/1.155 = 1.60$. If the angle is 90° then m(O—H) is $1.85/1.414 = 1.31$. In the same way $m(NH_3) = 1.5$. If the angles are tetrahedral m(N—H) = 1.5; if they are right angles, m(N—H) = 1.06. In view of the uncertainty of the deductions of the valence angles from wave mechanics,[46] it is here assumed that the angles are in all cases tetrahedral.

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[44] Pauling, *J. Am. Chem. Soc.*, 53, 1367 (1931).

Dipole Moments and the Periodic Classification

We are now in a position to form an estimate of the moments of individual links. Following the convention of Eucken and Meyer, the positive atom of the pair is always written first; and where carbon is concerned it is to be understood as a singly linked and not an unsaturated or aromatic carbon atom.

H—C. The value adopted for the moment of the H—C link affects those of nearly all the other links of carbon. There is good reason to think that it is small. Williams, and Eucken and Meyer,[47] have assumed that it is 0.4; it is at least probable that its value lies between 0.4 and zero. Sutton[48] has calculated the values of m(C—H) and m(C—Cl) from the observed moments of chloroform and methylene chloride,[49] and the observed angles between the C—Cl valences found by Bewilogua.[50] He makes two assumptions as to the angle between the C—H valences in methylene chloride: (a) that it is 109.5° as in methane, and (b) that it is reduced to 100° by the spreading of the C—Cl valences. He finds that m(H—C) is for (a) 0.15 and for (b) 0.20, the corresponding values for *m*(C—Cl) being for (a) 1.50 and for (b) 1.41. The moment of methyl chloride, as calculated from these values is (a) 1.65, and (b) 1.61. The observed value[51] is 1.86; the small discrepancy gives an idea of the magnitude of the effect of the moments of the links on one another, which is necessarily neglected in the calculations. In view of these conclusions of Sutton, it seems better to take the moment of H—C as 0.2.

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[45] This m(O—H) is a convenient symbol to express the phrase "the moment of the link O—H."

[46] Heisenberg, *Chemistry at the Centenary Meeting of the British Association* (Heffer, Cambridge, 1932), page 247.

[47] Eucken and Meyer, *Physik. Z.*, 30, 397 (1929).

[48] Sutton, *Proc. Roy. Soc. London*, 133, 689 note (1931).

[49] $CHCl_3 = 0.95$ and $CH_2Cl_2 = 1.59$, Sänger, *Physik. Z.*, 27, 556 (1926).

[50] Bewilogua, *Physik. Z.*, 32, 265 (1931). The angles between the C—Cl valences were found to be: in chloroform 116.4°, and in methylene chloride 123.8°.

H—N. The moment of ammonia is 1.46.[52] If we assume the tetrahedral angle between the N—H valences, this means that the moment of H—N is also 1.46.

H—P. The moment of phosphine is 0.55 (Watson);[52] hence *m*(H—P) = 0.55.

H—As. The moment of arsine has been found to be 0.15 (Watson).[52] So small a value would ordinarily be disregarded as being due to experimental error; but the work was carried out with great care over a temperature range from $-47°$ to $+99°$, and the effect of pressure was examined and allowed for, so that the moment may be taken as real. This of course gives H—As = 0.15.

H—O. The moment of water, according to the latest and most accurate measurements,[53] is 1.85. This gives, for an angle of 109.5°, H—O = 1.60.

H—S. From the moment of hydrogen sulphide, 0.93,[54] we get, for the angle 109.5°, the moment of H—S = 0.81.

H—F. The moment of H—F cannot be measured directly, owing to the polymerization of hydrofluoric acid in the gaseous state. The dielectric constant of liquid hydrofluoric acid is very large, being 174.8 at $-73°$ and 83.6 at 0°.[55] This indicates that the liquid contains highly polar molecules, but it is so highly polymerized that this gives little indication of the moment of H—F. We have seen, however, that the moment of ammonia is 2.6 times that of phosphine, and that of water twice that of hydrogen sulphide. If we assume similar angles for the two members of each pair, the ratios *m*(H—N) : *m*(H—P) and *m*(H—O) : *m*(H—S) will also be 2.6 and 2, respectively. We may suppose that a similar increase occurs when we pass from H—Cl (1.03) to H—F, and that the moment of the latter is somewhere between 1.5 and 2.0.

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[51] Sänger, *Helv. Phys. Acta*, 3, 161 (1930).

[52] Watson—*Proc. Roy. Soc. London*, 117, 43 (1927)—found 1.48; Keyes and Kirkwood, —*Phys. Rev.*, 36, 1570 (1930)—give 1.44. Gas, temperature.

[53] Sänger, *Physik. Z.*, 31, 306 (1930). Gas, temperature.

[54] Zahn and Miles, *Phys. Rev.*, 32, 497 (1928).

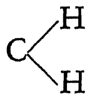
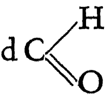
[55] Fredenhagen and Dahmlos, *Z. anorg. allgem. Chem.*, 178, 272 (1929).

H—Cl, H—Br, H—I. Hydrochloric, hydrobromic and hydriodic acids have been measured directly.[56] The values are: H—Cl = 1.03, H—Br = 0.78, H—I = 0.38.

C—N. The observed values of the moments of ammonia (1.46), methylamine (1.23), and trimethylamine (0.60),[57] show H_3C—N has a smaller moment than H—N (1.5). To obtain the value for C—N we have to allow for that of the CH_3 group, which we have seen to be the same as that of H—C (0.2). If we assume that the angles in trimethylamine are tetrahedral, we have 0.60 for H_3C—N, *i.e.* for $\overset{+\longrightarrow}{\mathrm{H—}}\mathrm{C}\overset{+\longrightarrow}{\mathrm{—N}}$. This gives 0.4 for C—N.[57a]

C≡N. The most probable value of the moment of methyl cyanide is 3.51.[58] Here again we have to allow for the H_3C, which makes C≡N = 3.3. The increase over the value of C—N is surprising, but we have no *a priori* reason to know what the effect of a multiple link will be.

C—O. The moment of methyl ether (1.32) gives, for an angle of 109.5°, H—C—O = 1.14 whence *m*(C—O) = 0.94. If the lower moment of dipropyl ether (0.86) is to be attributed wholly to the increase of the valence angle, the size of this angle in propyl ether must be 136°.

C=O. The dialkyl ketones all give moments very near to 2.75. Assuming, as we fairly may, that the molecule has a tetrahedral structure,  109°28′ and  125°16′, then the component of the H—C moments in the line of the C=O will be 0.23 so that *m*(C=O) = 2.5. Here again the double link has more than twice the value of the single.

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[56] Zahn, *Phys. Rev.*, 27, 455 (1926). Gas, temperature.

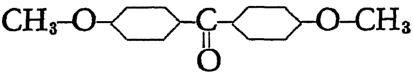
[57] Steiger, *Physik. Z.*, 32, 425 (1931).

[57a] There is however some reason to think that the true moment is higher than this, and may be as large as 0.7 or 0.8. See D. Ll. Hammick, R. G. A. New and L. E. Sutton, *J. Chem. Soc.* 1932, 745.

[58] Eide and Hassel, *Tids. Kemi Bergvesen*, 10, 93 (1930). Benzene, refraction.

$C\equiv O$. This link occurs in carbon monoxide, in the form that may be written $C\overset{\leftarrow}{\equiv}O$ or $\overset{-}{C}\equiv\overset{+}{O}$. We can thus arrive at a rather speculative value of the moment of the triple link of carbon to oxygen. The distance between the nuclei has been found to be 1.14Å (see p. 88). The transference of an electron through this distance will give rise to a moment of $1.14 \times 4.77 = 5.44$. The moment of carbon monoxide is 0.12.[59] Hence that of the triple link of carbon to oxygen is $5.44 \pm 0.12 = 5.56$ or 5.32. We may provisionally take the lower value.

$C—S$. The moment of diethyl sulphide is 1.57.[60] Assuming a tetrahedral angle, this gives the moment of $C_2H_5—S$, or $\overset{+\rightarrow}{H—C}\overset{+\rightarrow}{—S}$, as 1.36, whence $m(C—S) = 1.16$. If the thioethers behave like the ethers we should expect the angle of the sulphur valences in the ethyl compound to be rather larger than 109.5°, so this may be regarded as a minimum value. It will be noticed that it is definitely larger than $m(C—O)$.

$C=S$. We have three independent means of comparing the moments of $C=S$ and $C=O$, which give concordant results. The moment of phenyl isocyanate is 2.34 (Eide and Hassel),[58] and that of phenyl isothiocyanate is 2.76,[61] indicating that $m(C=S) - m(C=O) = 0.42$. This is supported by the observation of Wolf[62] that the moment of dianisyl ketone,  is 3.90, and that of the corresponding thioketone is 4.44, difference 0.54. Finally Zahn and Miles[54] have found the moment of carbon oxysulphide, a rectilinear molecule in which these two moments are balanced against each other, to be 0.65. The mean of these three differences—0.42, 0.54, and 0.65—is 0.54, so that we may take $m(C=S)$ to be 3.0.

$C—Se$, $C—Te$. Here the only values we have are those of diphenyl sulphide, selenide and telluride.[61] Values based on aromatic derivatives are somewhat uncertain, owing to the differences of moment between aryl and alkyl compounds (p. 179). If, however, we may assume that these similar aromatic derivatives differ among themselves in the same way as the alkyl compounds, we can calculate *m*(C—Se) and *m*(C—Te). The moments of these substances, and those of the C_6H_5—X groups calculated for an angle of 109.5° are:

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[59] Von Braunmühl, *Physik. Z.*, 28, 141 (1927); Forro, *Z. Physik*, 47, 430 (1928). Gas, temperature.

[60] Hunter and Partington, *J. Chem. Soc.*, 1931, 2062.

[61] Bergmann, Engel and Sandor, *Z. physik. Chem.*, B10, 397 (1930).

[62] Wolf, *Physik. Z.*, 31, 227 (1930).

$(C_6H_5)_2S = 1.47$ $C_6H_5—S = 1.27$
$(C_6H_5)_2Se = 1.38$ $C_6H_5—Se = 1.19$
$(C_6H_5)_2Te = 1.13$ $C_6H_5—Te = 0.98$

From this it follows that *m*(C—Se) = *m*(C—S) − 0.08, and that *m*(C—Te) = *m*(C—S) − 0.29. Taking the value given above of 1.16 for *m*(C—S), we get *m*(C—Se) = 1.08, and *m*(C—Te) = 0.87.

C—F. Here again we have to rely upon aromatic compounds, since no alkyl fluorides have been examined. There are three groups of data, which give very concordant results:

Radical	Chloride	Fluoride	Difference
Phenyl	1.59	1.42[63]	0.17
α-Naphthyl	1.59[64]	1.41[64]	0.18
β-Naphthyl	1.72[64]	1.56[64]	0.16

We may, therefore, take it that the moment of C—F is about 0.2 less than that of C—Cl, and since the latter is 1.7, *m*(C—F) = 1.5.

C—Cl, C—Br, C—I. The moments of these links can be got from the moments of the alkyl halides by subtracting that of H—C, which is 0.2. This gives:

$CH_3Cl = 1.9$ C—Cl = 1.7
$CH_3Br = 1.8$ C—Br = 1.6
$CH_3I = 1.6$ C—I = 1.4

The number of links not containing either hydrogen or carbon for which we have data is very small. A series of inorganic trihalides have been measured, and if they have a tetrahedral structure the moment of one link is of course equal to that of the whole molecule.

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[63] Walden and Werner, *Z. physik. Chem.*, B2, 10 (1929); Bergmann, Engel and Sandor, *ibidem*, B10, 106 (1930).

[64] Parts, *Z. physik. Chem.*, B10, 264 (1930).

These results are:

$\mathrm{PCl_3} = 0.80,$[65]
$\mathrm{AsCl_3} = 1.97,$[65]
$\mathrm{SbCl_3} = \left.\begin{array}{l} 3.64,^{66} \\ 4.06,^{65} \end{array}\right\}$ mean 3.9.

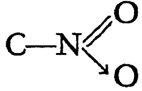
$\mathrm{PBr_3} = 0.61,$[65]
$\mathrm{AsBr_3} = 1.66,$[65]

$\mathrm{SbI_3}$ was found by Williams[67] to have a moment of 0.4, but this seems so improbable a value that we may suspend judgment until it has been confirmed.

N=O. Tertiary nitrosobutane has been found[68] to have a moment of 2.50. This is, therefore, the moment of $\overset{+\rightarrow}{\mathrm{H{-}}}\overset{+\rightarrow}{\mathrm{C{-}}}\overset{+\rightarrow}{\mathrm{N{=}}}\mathrm{O}$. Taking $m(\mathrm{H{-}C}) = 0.2$ and $m(\mathrm{C{-}N}) = 0.4$ we get $m(\mathrm{N{=}O}) = 1.9$.

The values for these various links are collected below in Table XXXVI, page 153.

Evidence for the Direction of the Moments

Williams' determination of direction from the mixed *para*-di-derivatives of benzene, on the practically certain assumption that the moment of the nitro group  $\mathrm{C{-}N}\begin{smallmatrix}\nearrow\!\!\!\!/\ \mathrm{O} \\ \searrow \mathrm{O}\end{smallmatrix}$ is directed away from the ring, establishes the directions of $\overset{+\longrightarrow}{\mathrm{C{-}Cl}}$, $\overset{+\longrightarrow}{\mathrm{C{-}Br}}$, $\overset{+\longrightarrow}{\mathrm{C{-}I}}$, $\overset{+\longrightarrow}{\mathrm{H{-}C}}$, $\overset{+\longrightarrow}{\mathrm{H{-}N}}$, and $\overset{+\longrightarrow}{\mathrm{C{-}CHO}}$ (from the aldehydes); that of $\overset{+\longrightarrow}{\mathrm{C{-}C{\equiv}N}}$ is proved by the low moment, 0.69, of *p*-nitrophenyl cyanide. The moments of the *p*-substituted phenols are ambiguous, and it is difficult to deduce from them the direction in C—O—H. But we can obtain the direction in H—O in another way. We know the direction $\overset{+\longrightarrow}{\mathrm{C{-}O}}$ from that of $\overset{+\longrightarrow}{\mathrm{C{=}O}}$, and we can calculate the moment of $\mathrm{H_3C{-}C{-}O}$ from that of methyl ether, as we have seen, which gives 1.14. We also know the value, though not the direction, of the H—O (1.61) from the moment of water. If we calculate assuming the tetrahedral angle, the moment of methyl ether from these values we find that if the H—O moment is directed towards the oxygen the total moment should be 1.65, which approximates to the observed moment. We can, therefore, conclude that in H—O the hydrogen is at the positive end.

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[65] Ebert, Eisenschitz and Von Hartel, *Z. physik. Chem.*, B1, 94 (1928).
[66] Werner, *Z. anorg. allgem. Chem.*, 181, 154 (1929).
[67] Williams, *Physik. Z.*, 29, 683 (1928).
[68] Hammick, New and Sutton, *J. Chem. Soc.*, 1932, 742.

We thus arrive at the following general conclusions with respect to the influence on the magnitude and direction of the moment, of the position in the periodic table of the atoms forming the link.

(1) In all ascertainable instances hydrogen in the link H—X is positive to X; and in the link C—X, except in C—H, carbon is positive to X; we do not however know the value of any link of carbon to an atom, other than hydrogen, in any of the first three periodic groups. This means that, wherever we can determine the direction, the atom belonging to the earlier periodic group—counting hydrogen as belonging to Group I—forms the positive member of the pair.

The application of wave mechanics to the problem has already led to this conclusion. Niessen, who had prevously[69] come to the opposite conclusion on the basis of the Bohr atomic model, has revised his view in the light of wave mechanics, and decided that the atom of lower atomic number will always form the positive member of the dipole.[70] It does not, however, appear to be possible, as yet, to calculate the moments in any detail by the methods of wave mechanics.

(2) Wherever the magnitudes are known it is found that the moments both of H—X and of C—X increase as X changes within any period from an earlier to a later group, C—N < C—O < C—F etc.; and also, with two exceptions, as X changes within a periodic group from a heavier atom to a lighter, H—As < H—P < H—N, P—Br < P—Cl, As—Br < As—Cl. The two exceptions are C—O, which has a smaller moment than C—S; and C—F, which

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[69] Niessen, *Physik. Z.*, 27, 300 (1926).
[70] Niessen, *ibidem*, 29, 52 (1928).

has a smaller moment than C—Cl. It will be noticed that the moment of H—C (0.2) is exceptionally low in comparison with H—N (1.5) and H—O (1.6), which may perhaps be connected with the fact that carbon differs from nitrogen and oxygen in having no unshared electrons in these compounds.[71]

(3) In all these cases we are dealing with a change of the negative atom, while the positive atom remains the same. When the negative atom is unchanged but the positive is replaced by a lighter atom from the same periodic group, then so far as our scanty data indicate we get the opposite effect and the moment diminishes:

$$\text{Sb—Cl} > \text{As—Cl} > \text{P—Cl}, \quad \text{As—Br} > \text{P—Br}.$$

(4) With multiple links the moment increases more rapidly than the number of links, as the following tabulation shows:

	μ	Ratio		μ	Ratio		μ	Ratio
C—N	0.4	1	C—O	0.9	1	C—S	1.2	1
C=N	—	—	C=O	2.5	2.8	C=S	3.0	2.5
C≡N	3.3	8.2	C≡O	5.3	5.9			

TABLE XXXVI

Dipole Moments of Individual Links

H—C	0.2	H—N	1.5	H—O	1.6	H—F	(2)
		H—P	0.55	H—S	0.8	H—Cl	1.03
		H—As	0.15			H—Br	0.78
						H—I	0.38
		C—N	0.4	C—O	0.9	C—F	1.5
				C=O	2.5		
		C≡N	3.3	C≡O	5.3		
				C—S	1.2	C—Cl	1.7
				C=S	3.0		
				C—Se	1.1	C—Br	1.6
				C—Te	0.9	C—I	1.4
P—Cl	0.8	P—Br	0.6				
As—Cl	2.0	As—Br	1.7				
Sb—Cl	3.9						
		N=O	1.9				

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[71] For a parallel instance see page 120.

A knowledge of the moments of individual links enables us to calculate the distribution in the molecule of the residual charges due to the unequal sharing of the linked electrons. To take the simplest example, that of a diatomic molecule, in hydrogen chloride the moment is 1.03 and the distance between the nuclei 1.27Å. The moment is the product of one of the residual electrical charges into the distance between them. If we regard these charges as located on the nuclei, which it is quite permissible to do, each charge must be equal to $1.03/1.27 = 0.81 \times 10^{-10}$ electrostatic unit. It is more convenient to express this charge, not in absolute units, but as a fraction, F, of the charge 4.77×10^{-10} of an electron; thus for H—Cl $F = \pm 0.81/4.77 = \pm 0.170$. Similar calculations may be made for any link of which we know the length and the moment. The values of this fraction F, for a series of the more important links, are given in Table XXXVII where, as before, the positive atom of the link is always written first.

With the help of these values we can find the distribution of the residual charges in any molecule formed of these links. The results are, of course, only a first approximation to the truth. Even if our values of the dimensions and the moments are accurate, we are taking no account of the inductive effect of the moments on one another; and in dealing with aromatic compounds the results will be still further modified by the "electromeric" effect discussed below on page 178. But as a rough measure of the electrical state of the molecule these calculations are not without interest.

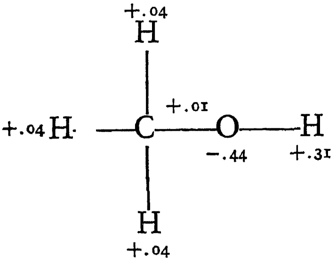
Where an atom forms several links the charges acquired from each must, of course, be added together. For example, in methyl alcohol each methyl hydrogen has $F = +0.04$, and hence from the three C—H links the carbon has a charge of -0.12. From the C—O the carbon gains $+0.13$, so that its total charge is $+0.01$. The oxygen has -0.13 from the C—O and -0.31 from the O—H, or -0.44 in all. The hydroxyl hydrogen has $+0.31$. When the molecule has an ionic charge or contains a co-ordinate link, the value $F = 1.0$ must be added to or subtracted from the appropriate atom. A co-ordinate link gives the donor $+1.0$ and the acceptor -1.0. With an ion, if there is any doubt where the ionic charge should be put, this is easily found by counting the number of electrons to each atom, a shared electron being counted as half. For example, in the NH_4 ion each hydrogen has two shared electrons to balance its nuclear charge of $+1$, and so as a first approximation, on the assumption of an equal sharing of the electrons is neutral. The nitrogen, which needs 5 electrons in the outer group for neutrality, has 8 shared electrons, which are equivalent to 4 unshared; this gives it a charge of $+1$, which is the ionic charge. The residual charge, due to the unequal sharing of the electrons of the link, must then be added.

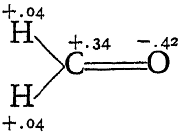
TABLE XXXVII

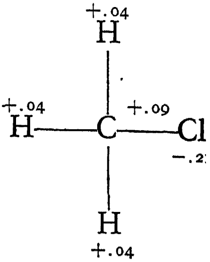
Residual Charges

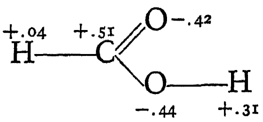
Link	Moment $= \Delta E \times d$	Distance d	ΔE	$\Delta E/e = F$
H—C	0.2	1.14	0.18	0.04
H—N	1.5	1.08	1.4	0.29
H—O	1.6	1.07	1.5	0.31
H—S	0.8	1.43	0.6	0.13
C—N	0.4	1.48	0.3	0.06
C≡N	3.3	1.15	2.9	0.61
C—O	0.9	1.47	0.6	0.13
C=O	2.5	1.27	2.0	0.42
C—S	1.2	1.83	0.7	0.15
C=S	3.0	1.59	1.9	0.40
C—Cl	1.7	1.74	1.0	0.21
C—Br	1.6	1.90	0.8	0.17
C—I	1.4	2.12	0.7	0.15
(N—O	0.5 ?	1.41	0.4	0.08 ?
N=O	1.9	1.21	1.6	0.34)

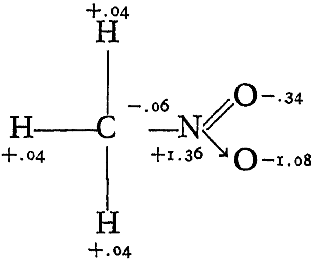
A few examples of the application of these principles are given below:

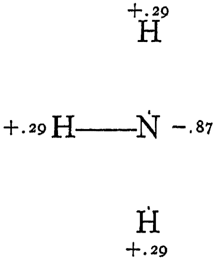


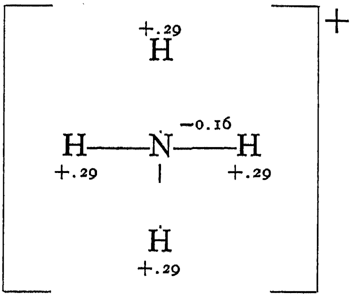










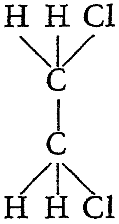


Flexible Molecules

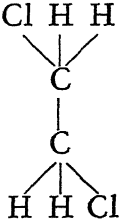
The investigation of this problem has led to results of considerable interest in their bearing on the configuration of molecules in general. Flexible molecules, as we have seen, are those the moments of which may vary owing to the rotation of atomic groups about the line of a single link.

The possibility of such "free rotation" for singly linked atoms was one of van 't Hoff's fundamental principles of stereochemistry. We must, however, be clear as to what the principle exactly means. It was founded upon the non-existence of isomers whose structures could pass into one another by means of such rotation; it did not assume that the rotation went on continuously in the molecule, or that all the positions to which it could lead were equally favorable.

As a simple example we may take ethylene dichloride:

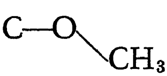
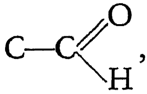


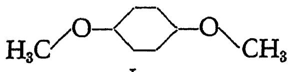
I



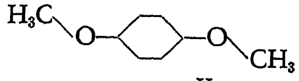
II

If we assume the lower CH_2Cl group to be at rest, it is possible for the upper group to take up any position between *I*, where the Cl atoms are directly over each other (almost as in *cis*-dichloroethylene), and *II* where they are as far removed as possible (as in the *trans* compound). The principle of free rotation requires that out of all the possible positions there should not be two of sufficient stability for molecules to remain permanently in each, without passing over to the other. If they could do so compounds of the type of ethylene dichloride would exist in two isomeric forms, which they are not found to do. But whether such a molecule passes continuously from one position to another or remains more or less permanently in one of them, cannot be decided by chemical evidence alone.

The problem is obviously one on which the study of dipole moments may be expected to throw light. Of the two positions given above, *I*, the "*cis*" position will have a considerable moment, while *II* will be non-polar. Attention was directed to the subject through the moments found for certain *para* disubstitution products of benzene. As we have seen, such a compound, if the two substituents are the same, should have zero moment, and many of them, *e.g.* p-$C_6H_4Cl_2$, p-$C_6H_4Br_2$, p-$C_6H_4(CH_3)_2$, are non-polar. But it was found that certain compounds of this type have definite and sometimes quite large moments: for example, $p\text{-}C_6H_4(O{\cdot}CH_3)_2 = 1.74$, $p\text{-}C_6H_4(CH_2Cl)_2 = 2.23$, and $p\text{-}C_6H_4(CHO)_2 = 2.35$. The explanation is apparent when we notice that in the first series the resultant moment of the substituent, C—Cl, C—CH₃, lies in the central line of the molecule; while in the second series,  $C{-}O{-}CH_3$,  $C{-}C(=O)H$, it does not. It is therefore possible for molecules of the second kind to assume different configurations by the rotation of these unsymmetrical groups about the single link to the ring, without any deformation of the valence angles. For example, quinol dimethyl ether may assume any form between:


I

and


II

of which *I* is polar and *II* is non-polar.

Eucken and Meyer[72] calculated the moments of the most polar and the least polar forms of several of these flexible molecules, and showed that the observed values fell between these limits. For example, they found for:

	max.	min.	obsd.
ortho-cresol,	1.9	1.2	1.45
methyl acetate,	3.4	1.1	1.7

In a later paper Meyer[73] has pursued the subject further. It is evident that the most favored position will be that in which the potential energy, and hence the dipole moment, is at a minimum.[74] The extent to which the molecules are deflected from this position will depend on the relative magnitudes of two opposing influences. The first of these is the work required to cause the deflection, which is the intramolecular potential of the moments; and the second is the energy of the thermal agitation, which is of course proportional to the temperature. If the potential is much larger than this thermal energy, the molecule will remain practically undisturbed in its position of minimum (in a symmetrical molecule such as ethylene dichloride, of zero) moment. If, however, the thermal energy is much greater than the potential, then the latter will have only a negligible effect, and the molecule will assume all possible positions with equal frequency.

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[72] Eucken and Meyer, *Physik. Z.*, 30, 397 (1929).

[73] L. Meyer, *Z. physik. Chem.*, B8, 27 (1930).

[74] This is true for relatively simple molecules; but another factor, that may arise in certain types of molecules is a steric interference of large groups with one another. This may for the present be disregarded; but examples of its occurrence will be given on page 163.

With a molecule like ethylene dichloride, $CH_2Cl—CH_2Cl$, which has two similar groups with a single link between them, if the moment of each group (here practically that of the link C—Cl) is μ_1, we shall have:

Minimum moment,	0
Maximum moment,	$1.89\mu_1$
Mean moment for completely free rotation,	$\sqrt{2}\mu_1 = 1.41\mu_1$

If the thermal energy is either much greater or much smaller than the potential, its change with temperature over the range usually investigated will have no effect on the moment. Thus we have three possible cases, *A* being potential and B thermal energy:

(I) $A \gg B$; $\mu = 0$; temperature coefficient $= 0$.
(II) A ca. $= B$; $0 < \mu < \sqrt{2}\mu_1$; temperature coefficient finite.
(III) $A \ll B$; $\mu = \sqrt{2}\mu_1$; temperature coefficient $= 0$.

Now the potential of two moments, μ_1, μ_2, at a distance d apart, can be shown to be approximately $\mu_1\mu_2/d^3$. The thermal energy is kT where k is the gas constant R divided by the Avogadro number N, and for a molecule at the ordinary temperature it amounts to 4×10^{-14} erg. Calculation shows that if the potential is less than kT/10 it will not interfere perceptibly with the freedom of rotation, and the moment will have the statistical mean value $\sqrt{2}\mu_1$. Since the moments are of the order of 1×10^{-18} electrostatic unit, it follows that if the thermal energy is to equal the potential:

$$4 \times 10^{-14} = \mu^2/d^3$$
$$= (10^{-18})^2/d^3$$

or

$$d^3 = 0.25 \times 10^{-22}$$
$$d = 3 \times 10^{-8}\text{cm}.$$

This is of the order of twice the distance between two linked atoms in an organic molecule.[75] Thus it is evident that when the dipoles are near together we may expect the moment to be reduced below the mean statistical value through the interference of the intramolecular potential; but when they are far apart it should reach that value.[76]

The details of Meyer's calculation of the potential in individual molecules are complicated, and in one respect, the position that he assigns to the center of the dipole, are not entirely satisfactory;[77] but this is of little importance, as the whole calculation is only approximate. We may consider three examples which he develops in detail. In the *para* di-derivatives of benzene with flexible groups, such as quinol dimethyl ether, the distance between the dipoles, which are separated by the whole diameter of the benzene ring, is some 6Å. Hence, as the above calculation shows, the potential will be too small to interfere with the rotation, and the moment will have its full (mean) value.[78] An example of the other extreme is the carboxyl group, where the proximity of the highly polar C=O group to the hydroxyl (the flexible group) gives the high potential of about 10*k*T, which means that the rotation would become completely free only at about 20,000°. The hydrogen will thus be held permanently in the position of minimum moment.

Between these extremes will come the molecules in which the potential is of the same order as the thermal energy; these should show a variation of moment with

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[75] For $\mu = 0.5$, $d = 1.8$Å; for $\mu = 4$, $d = 7$Å.

[76] For a further discussion of this question see: Smyth, Dornte and Wilson, *J. Am. Chem. Soc.*, 53, 4242 (1931).

[77] Meyer assumes—see reference 73, its page 30—that all the free as well as the two shared electrons of the valence group of each atom, contribute equally to the moment. Thus in HCl (H contributing one electron and Cl seven) the center of the dipole is taken to be 1/8 of the H—Cl distance from the chlorine, and the same with C—Cl; in C=O (C giving two and O six) it is 1/4 from the oxygen. This seems to involve an unproved and rather doubtful theory of the mechanism of the moment.

[78] Weissberger and Sängewald—*Physik. Z.*, 30, 792 (1930)—find that whereas the moments of the dialkyl ethers fall with increase of the alkyl groups, those of the quinol ethers are practically constant:

dimethyl	1.81	di-*n*-propyl	1.79
diethyl	1.76	di-*n*-octyl	1.73

They consider that the benzene ring, on account of its shape, has no steric interaction with the alkyl groups.

temperature. A substance that appears to come in this intermediate class is ethylene dichloride, for which the potential is between two and three times kT for ordinary temperatures. The temperature coefficient of its moment has been the subject of a number of papers;[79] the facts have been disputed, but it is now clear that they support the theory. The configuration of this molecule has been examined by Debye by the method of X-ray scattering.[80] He finds that the *trans* position, with a distance of 4.4Å between the chlorine atoms, is the most favored; but the curves indicate that the molecules are partly displaced by the thermal agitation from this position, and to an extent which accounts satisfactorily for the observed moment of about 1.3.[80a]

With the corresponding dibromides, Smith and Kamerling[81] have obtained clear evidence of the effect of temperature on the freedom of the rotation. They measured the ethylene and the tri-, penta-, and decamethylene compounds—$Br(CH_2)_nBr$, where $n = 2, 3, 5, 10$—at a series of temperatures; owing to the real change of moment with temperature it was necessary to correct for P_E by means of the refraction. The results obtained in heptane solution were:

	−30°	−10°	+10°	+30°	+50°	+70°
2	0.79	0.94	0.98	1.04	1.05	1.05
3	2.07	2.11	2.15	2.18	2.19	—

	−40°	−20°	0°	+20°	+40°	+60°	+80°
5	2.28	2.34	2.39	2.43	2.47	2.48	—
10	—	—	2.69	2.73	2.75	2.76	2.75

These show clearly how the lengthening of the chain, and the increase of the distance between the polar links, gives the groups a greater freedom; the moment increases and the temperature coefficient falls.

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[79] Meyer, *Z. physik. Chem.*, B8, 27 (1930); Sänger, *Physik. Z.*, 32, 21 (1931); Meyer, *ibidem*, 32, 260 (1931); Smyth and coworkers, *J. Am. Chem. Soc.*, 53, 527, 2005, 2988, 4242 (1931).

[80] Debye, *Physik. Z.*, 31, 142, 419 (1930).

[80a] Some evidence has recently been produced to show that the molecules are partly in the *cis* configuration, owing presumably to the van der Waals attraction between the chlorine atoms. See K. W. F. Kohlrausch, *Z. physik. Chem.*, B18, 16 (1932); A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, *Monatsh*, 60, 221 (1932).

[81] Smith and Kamerling, *J. Am. Chem. Soc.*, 53, 2988 (1931).

An interesting question from this point of view is the behavior of the optically active and *meso* forms of compounds of the tartaric acid type, Cabc—Cabc. For completely free rotation the two forms should have the same moment, so that any difference in the moment would indicate some restraint; the structures are too complicated for any more quantitative statement to be possible. Three such pairs have been examined: hydrobenzoin and isohydrobenzoin,[82] diethyl *dextro-* and *meso*-tartrate,[83] and the two forms of stilbene dichloride.[84] The values are given in Table XXXVIII.

TABLE XXXVIII

		μ
Hydrobenzoin, $C_6H_5 \cdot CHOH—CHOH \cdot C_6H_5$		2.08
Isohydrobenzoin, $C_6H_5 \cdot CHOH—CHOH \cdot C_6H_5$		2.67
Diethyl *dextro*-tartrate,	12°	3.09
	38°	3.16
Diethyl *meso*-tartrate,	12°	3.66
	38°	3.69
α-Stilbene dichloride, $C_6H_5CHCl—CHClC_6H_5$		1.27
β-Stilbene dichloride,		2.75

With hydrobenzoin it was at first supposed that the moments were nearly the same, indicating almost completely free rotation; but later work has shown that they differ by about 25 per cent. In the tartaric esters there is a difference of about 18 per cent, and the active form, which appears to be the more restrained, shows the rise of moment with temperature which is to be expected, although the range of temperature is too small for this to be certain. These two pairs are not very suitable for this investigation owing to the additional complication introduced by the two hydroxyl groups, which may be associated in the chemical sense; indeed, as Lowry[85] has pointed out, the tartaric ester molecule may form a double chelate ring by the co-ordination of each C=O group with the hydrogen of the β-hydroxyl. The two stilbene compounds, which are formed from the hydrobenzoins by treatment with phosphorus pentachloride, have no hydroxyl groups and so are not subject to this complication, and might be expected to have a greater freedom of rotation. Instead of this, however, their moments show a difference of quite another order (2.2:1). This suggests that with these compounds the main factor in determining the potential may be the steric effect of the two phenyl groups, which may cause the position of minimum energy in either the racemic or the *meso* form to be one of considerable moment.

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[82] Weissberger and Sängewald, *Z. physik. Chem.*, B12, 399 (1931); Hassel and Naeshagen, *ibidem*, B14, 232 (1931).

[83] K. L. Wolf, *Trans. Faraday Soc.*, 26, 315 (1930).

[84] Weissberger and Sängewald, *Z. physik. Chem.*, B9, 133 (1930).

[85] Lowry, *Trans. Faraday Soc.*, 26, 352 (1930).

Dipole Moment and Co-ordination

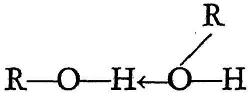
It is generally agreed that the co-ordinate link, to which Werner first drew attention, is a covalent link formed in an unusual way; it consists of two shared electrons, but both are derived from the same atom:

$$\begin{array}{rcr} A^{\cdot} + .B = A{:}B & \qquad\qquad & A{:} + B = A{:}B \\ A\text{—}B & & A\rightarrow B \end{array}$$

Normal *Co-ordinate*

Covalence

The formation of the co-ordinate link thus requires the simultaneous presence of two atoms, one with a pair of unshared valence electrons to lend (the donor) and another (the acceptor) with a valence group that can increase by two. The simplest example is the association of the hydroxyl group:



$$\mathrm{R{-}O{-}H \leftarrow \overset{R\,\diagup}{O}{-}H}$$

The oxygen, the donor, has 8 valence electrons of which 4 are already shared, and the acceptor, hydrogen, has two shared valence electrons, but it can carry four.

In practice it is found that this requirement is always fulfilled; co-ordination never occurs except between atoms that satisfy these conditions.

But the conditions, though necessary, are not sufficient. We often find that two such atoms may be present without co-ordination taking place; there is evidently some further condition that must be fulfilled before the link can be formed.

The facts are most fully worked out in relation to the acceptor properties of hydrogen. The ordinary 1-covalent hydrogen atom can increase its valence group to 4, and so should be capable of co-ordination; but we find that while hydrogen attached to oxygen readily forms the link, hydrogen attached to carbon in a saturated compound never does so at all. We can, in fact, discover a regular relation between the acceptor properties of hydrogen, and the position in the periodic table of the atom to which it is attached. We may consider these elements in order.

In H—H there is no evidence of co-ordination at all.

In H—C the acceptor properties of the hydrogen atom are almost if not quite negligible, at any rate when the carbon is saturated. The structure of the addition compounds of ethylene and the aromatic hydrocarbons is very obscure, and there is always a possibility that the double links may play a part in their formation; but if we confine ourselves to saturated compounds—paraffins and alkyl groups—there is no evidence of co-ordination.[86]

With H—N we have more evidence, but even here the tendency is weak. This is shown by the very small association of ammonia as compared with water. The strong donor power of the nitrogen in ammonia is proved by the existence of the innumerable metallic ammines, and the ammonia molecules are obviously prevented from associating only by the weak acceptor power of their hydrogen atoms. A clear case of the co-ordination of hydrogen attached to nitrogen is afforded by the hydroxides of the primary, secondary and tertiary ammines. It has been shown[87] that an aqueous solution of these ammines contains a considerable amount of the hydrate, R_3NHOH, along with a good deal of anhydrous base, R_3N, and a small concentration of ions. Thus the molecule R_3NHOH is a weak electrolyte, and is present mainly in the covalent form, which can only have the structure $R_3N—H \leftarrow O—H$.[88] But here the conditions are exceptionally favorable for co-ordination; the negative charge of the donor and the positive charge of the acceptor will both promote the reaction, the linking electrons being repelled from the donor and attracted towards the acceptor.

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[86] The solid hydrate of methane, $CH_4,6H_2O$—de Forcrand, *Compt. rend.*, 135, 959 (1902)—is obviously not a valence compound, but, like the hydrates of argon, krypton and xenon, a crystalline aggregate in which the molecules are held together by van der Waals forces.

[87] Moore, *J. Chem. Soc.*, 91, 1373 (1907); Moore and Winmill, *ibidem*, 101, 1635 (1912).

In H—O the hydrogen accepts very readily. Hydroxyl is the typical associating group, with a strong donor and a strong acceptor, and it is present in the great majority of associated substances.

In H—F the tendency to co-ordination is even stronger. This is somewhat concealed by two facts: the univalency of fluorine limits the number of examples: there are many compounds R—O—H, but only one H—F; and the small size and single charge of the fluorine ion make ionization very easy. But the readiness with which hydrofluoric acid polymerizes even in the vapor, and forms the co-ordinated ion $[F \rightarrow H—F]^-$ in solution, shows that the hydrogen has a strong tendency to act as acceptor. The same thing is proved by the existence of complex acid fluorides containing the group $M—F \rightarrow H—F$.

Thus the tendency of the hydrogen to act as acceptor increases in the order:

$$H—C < H—N < H—O < H—F.$$

In combination with elements of the second short period (Na–Cl) hydrogen shows scarcely any co-ordinating power at all. With H—Si and H—P our information, owing to various complicating factors, is scanty, but no sign of the co-ordination of hydrogen in these positions has been observed.

With H—S the position is clear. Neither hydrogen sulphide nor the mercaptans are in any degree associated; and that this is not due to any weakness of the donor power of the sulphur is shown by the numerous co-ordination compounds (with sulphur as donor) formed by hydrogen sulphide, the mercaptans and the thioethers. It is evident that when we pass from H—O to H—S the acceptor power of the hydrogen practically vanishes.

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[88] This structure was proposed by Latimer and Rodebush, *J. Am. Chem. Soc.*, 42, 1419 (1920).

The same thing happens when we pass from H—F to H—Cl. Hydrochloric acid shows no signs of association: there is some evidence for the existence of complex salts with the group M—Cl→H—Cl, but they are doubtful, and in any case rare; and while the donor power of chlorine is less than that of iodine, there is no reason to think that it is less than that of fluorine.

Thus the chemical evidence shows that the acceptor properties of a hydrogen atom change regularly with the position in the periodic table of the atom to which it is attached: they increase as this changes from left to right (C to F), and fall off as we go from the first to the second period.

This is precisely the way in which the dipole moment of the link changes, and so it seems that the acceptor power of a hydrogen atom in any link increases with the moment of the link.[89] This is what we should expect. In all these links the hydrogen is positive, and the energy that it evolves in taking a share in a new pair of electrons, must be greater, the larger its positive charge. The calculations given above (see Table XXXVII, p. 155) show that the positive charge of the hydrogen in these links, if we may accept the extrapolated estimate of 2.0 for the moment of HF, is:

H—C 0.04	H—N 0.29	H—O 0.31	H—F 0.46
		H—S 0.13	H—Cl 0.17

At the same time these figures show that the relation between the charge and the co-ordinating power is not exact, and that the latter must be influenced by other factors as well.

The formation of the undissociated R_3N—H←O—H illustrates a further effect of the ionization. Before co-ordination the ammonium hydrogen has the same charge of +0.29 as it has in ammonia; the oxygen has a negative charge of 1.31; and in addition the opposite ionic charges on the two molecules will promote their combination by greatly increasing the probability of their meeting one another.

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[89] Sidgwick, *Z. Elektrochem.*, 34, 445 (1928).

It has been urged as an objection to this theory of co-ordination, that the assumed transference of an electron from one atom to another involves a disturbance of the electrostatic equilibrium of which there is no evidence. But the measurement of the moments of molecules containing co-ordinate links has strongly confirmed the theory, by showing that this disturbance does in fact occur. In the "divalent carbon" compounds,[90] such as carbon monoxide and the isocyanides, there is evidence of a co-ordinate link in which the carbon is the acceptor: $O\overset{\rightarrow}{=}C$, $R{-}N\overset{\rightarrow}{=}C$. In carbon monoxide, as we have already seen (p. 149) this assumption leads to a probable value of the inequality of sharing of the 6 electrons common to the two atoms. In the isocyanides we can calculate from the moments what the distance should be through which the electron is transferred. The moment of phenyl isocyanide $\overset{+-}{C_6H}\ \overrightarrow{-N\overset{\rightarrow}{=}C}$ (3.5) is 0.4 less than that of phenyl cyanide $\overset{+}{C}_6H_5{-}C{\equiv}N$ (3.9). Since we have found that the moment of $\overset{+\longrightarrow}{C{-}C{\equiv}N}$ is 3.3, we may assume that of $\overset{+\longrightarrow}{C{-}N\overset{\rightarrow}{=}C}$ to be 2.9. This latter is made up of three moments: (1) that of $\overset{+\longrightarrow}{C{-}N}$ (0.4); (2) that of $\overset{\longleftarrow+}{N{\equiv}C}$ (3.3); (3) that of the transferred electron of the co-ordinate link (+→) which is 4.77*d*, where *d* is the distance between the carbon and the nitrogen atoms; this third moment exceeds the sum of the other two by the moment of the whole group, 2.9. Hence we have:

$$\begin{array}{c} 4{\cdot}77d \\ C{-}\overset{+\longrightarrow}{N\overset{\rightarrow}{=}C} \\ \overset{+\rightarrow}{}\quad\overset{\leftarrow+}{} \\ 0{\cdot}4 \quad 3{\cdot}3 \end{array}$$

$$\begin{aligned} 4{\cdot}77d + 0{\cdot}4 - 3{\cdot}3 &= 2{\cdot}9 \\ 4{\cdot}77\,d &= 5{\cdot}8 \\ d &= 1.21\text{Å} \end{aligned}$$

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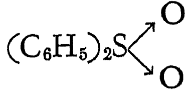
[90] See below, page 187.

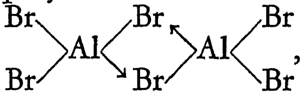
Thus the moments indicate a distance of 1.2Å between the triply linked carbon and nitrogen atoms in the isocyanides. This distance has not been measured,[91] but we should expect it to be much the same as that between the triply linked carbon atoms in acetylene, which is 1.19Å, or between the triply linked nitrogens in nitrogen gas, which is 1.10Å.

Further support is given by the large moments that have been observed in a number of compounds known to contain co-ordinate links. Thus we have for the sulphoxides and sulphones:

Diphenyl sulphoxide	$(C_6H_5)_2S \rightarrow O$	4.08[92]; 4.17[93]
Dibenzyl sulphoxide	$(C_7H_7)_2S \rightarrow O$	3.88[92]
Diphenyl sulphone	 $(C_6H_5)_2S{\nearrow O \atop \searrow O}$	5.05[93]

Still larger moments are given by a series of co-ordination compounds of the halides of beryllium, boron and aluminum;[94] for example:

$BeBr_2$,	$2(C_2H_5)_2O$	7.57
BCl_3,	CH_3CN	7.65
$AlCl_3$,	$(C_2H_5)_2O$	6.54
$AlCl_3$,	$C_6H_5NO_2$	9.05
$AlCl_3$	$(C_6H_5)_2CO$	8.72

The behavior of aluminum bromide is remarkable.[95a] It is, of course, polymerized to Al_2Br_6 in the vapor, and presumably in nonionizing solvents also at the ordinary temperature. In carbon bisulphide its moment was found to be very small, 0.0 and 0.6, and it is probably non-polar. If the polymerized form has the structure usually attributed to it, , this is to be expected. In benzene it appears to be non-polar in the less dilute solutions; but when the concentration falls to less than 0.005N the molecular polarization begins to increase rapidly, and the extrapolated value for infinite dilution corresponds to a moment for $AlBr_3$ of 4.89. Ulich explains this by supposing that in carbon bisulphide it remains as the double polymer down to extreme dilution, while in benzene it begins at the lowest concentrations to dissociate into $AlBr_3$. There are two objections to this. In the first place, there is no apparent reason why there should be this difference in the behavior of the two non-associated and non-polar solvents; in the second place, the value obtained for the moment is much larger than we should expect for $AlBr_3$, as may be seen by comparing it with the moments of PBr_3 (0.61) and $AsBr_3$ (1.66); it is of the order observed with molecules containing a co-ordinate link. It seems more probable that the aluminum bromide has some tendency to form a co-ordination compound with the benzene, and that this is the compound whose moment is measured. If we have the simultaneous reactions:

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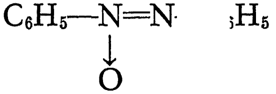
[91] From the band spectrum of cyanogen it has been calculated the distance for the triply linked C≡N is 1.15 Å.—Mecke, *Bandspektra und ihre Bedeutung für die Chemie* (Berlin, 1929), p. 23.
[92] Bergmann, Engel and Sandor, *Z. physik. Chem.*, B10, 397 (1930).
[93] De Vries and Rodebush, *J. Am. Chem. Soc.*, 53, 2888 (1931).
[94] Ulich and Nespital, *Z. angew. Chem.*, 44, 750 (1931).
[95a] Ulich and Nespital, *Z. Electrochem.*, 37, 559 (1931).

$$AlBr_3 \cdot C_6H_6 \rightleftharpoons AlBr_3 \rightleftharpoons Al_2Br_6$$

occurring, it is obvious that as the concentration diminishes, the equilibrium will tend to pass over to the left-hand side.

It should be mentioned that there is an unexplained exception to the rule that molecules with co-ordinate links have large dipole moments. Azoxybenzene, which undoubtedly has the formula



$$C_6H_5\text{—}\underset{\substack{\downarrow\\ O}}{N}{=}N\cdot \quad ;H_5$$

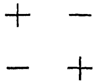
has a moment of only 1.8. Its derivatives *para*-azoxyanisol and *para*-azoxyphenetol also have low moments of 2.3, in spite of the contribution which the flexible alkyloxy-groups must make to the moments.[95b] No reason for this exception has been suggested, and no parallel instances are known.

[95b] Moments calculated by K. Höjendahl, *Studies of Dipole Moments* (Copenhagen, 1928) from the measurements of L. Ebert and H. von Hartel, *Physik. Z.*, 28, 786 (1927).

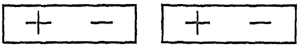
Another phenomenon that supports the view that coordination compounds have large dipole moments is the form of the curve relating molecular polarization to concentration which is found for alcohols in non-polar solvents. This will be discussed in the next section.

Dipole Association

As we have seen, it is necessary for the determination of the moments that the polar substance should be measured in a state of extreme dilution, either as a gas or in dilute solution in a non-polar solvent. Unless they are far removed from one another the dipoles exert a mutual effect, and the extent of this cannot be calculated. In stronger solution the equations relating the moment to the polarization break down, and the molecular polarization is no longer independent of the concentration. The change must be due to some orientation of the dipoles, and this is what is meant by dipole association. Debye pointed out some time ago[96] that we can imagine various forms of attachment of the dipoles to one another, of which some will diminish and others increase the polarity, as in the two simple examples, *I* and *II*, herewith:



I



II

In *I* the dipole moment is reduced to zero if the approach is close enough. In *II* the molecular polarization of the dimeric dipole is 4 times that of the simple dipole; but as the polymerization reduces the number of dipoles in the solution to half, the effect is only to double the polarization. Since, however, the moment is proportional to the square root of the polarization (page 130), the result of complete conversion into double dipoles of Type *II* would be to increase the moment as calculated by the factor $\sqrt{2}$. The first kind of association, with reduction of the polarization, is obviously to be expected; but the second type seems improbable without the help of other forces in addition to the electrostatic attraction of the dipoles; for without such help this Type *II* is evidently unstable, and any displacement from the straight line, such as must be produced by the thermal agitation, will lead to its changing over into Type *I*. The whole problem is obviously very complicated; the approach of the dipoles to one another will be restricted in many molecules by the steric interference of the attached groups of atoms, and thus the magnitude of the effect will depend not only on the moment of the dipole but also on its position in the molecule.

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[96] Debye in Marx's *Handbuch der Radiologie* (Leipzig, 1926), Vol. VI, page 597.

Experimentally this mutual interaction of dipoles can be observed by measuring the change of molecular polarization of a polar solute in a non-polar solvent as the concentration varies from extreme dilution up to the pure solute. Such measurements give two types of curve. In the most frequent, the polarization falls off steadily with increasing concentration: with nitrobenzene, for example, from 348 cc at infinite dilution to 94 cc for the pure liquid; if we subtract the optical polarization, which is constant, of 39 cc, this means that the dipole polarization falls from 309 to 55 cc, or in the ratio of 5.6 to 1. This is an extreme case; the fall is usually smaller, the ratio being commonly between 1.5 and 2.51;[97] with some polar substances it is much smaller than this, ethyl ether showing scarcely any change at all. With another class of substances, chiefly the lower alcohols, quite a different type of curve is obtained, in which the molecular polarization increases from infinite dilution up to a certain concentration, and then falls, ultimately to a lower value than that at which it started. It is simpler to discuss the two types of curve separately.

The normal type of curve, Figure 7, *I*, occurs with substances like nitrobenzene which in the pure state do not behave as associated liquids.[98] It is, therefore, presumably due rather to a mutual attraction of the dipoles than to any chemical combination or co-ordination; but it may be caused either by an aggregation of the polar molecules into groups of two or more, or to their orientation throughout the liquid. In the well marked instance of nitrobenzene in benzene, it was pointed out by Höjendahl[98] that the cryoscopic results show a corresponding change with concentration. A more detailed comparison of recent data,[99] both for the polarizations and the freezing points, confirms this conclusion. On the hypothesis that nitrobenzene forms non-polar double molecules, we can calculate their proportion at any concentration, on the one hand from the freezing point and on the other from the molecular polarization. For concentrations up to about 1 mole per liter, the values obtained by these two methods

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[97] Errera, *Leipziger Vorträge*, 1929, p. 107.

[98] Höjendahl, *Studies of Dipole Moments* (Copenhagen, 1928), p. 34. Sack, *Ergebnisse Exakten Wissenschaften*, 8, 315 (1929). Debye, *Polar Molecules* (London, 1929), p. 47. Errera, *Z. physik. Chem.*, 138, 332 (1928); *Leipziger Vorträge*, 1929, pp. 27, 109. Smyth, *Dielectric Constant and Molecular Structure* (New York, 1931) p. 180.

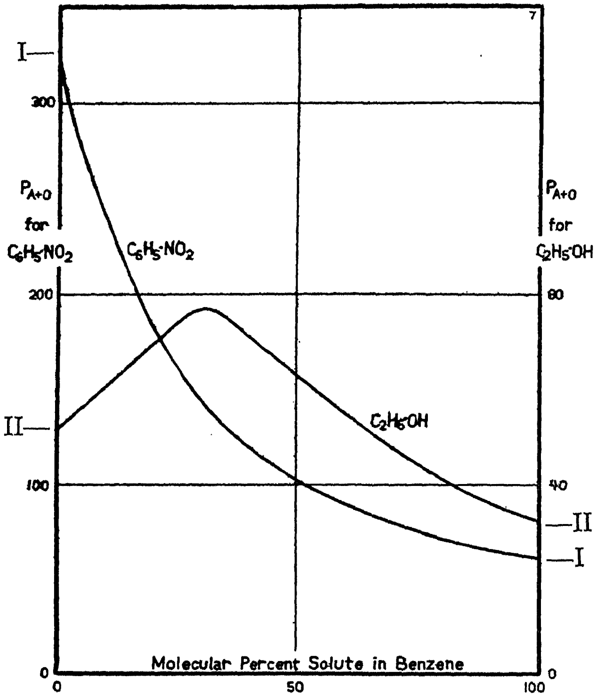

FIG. 7. Dipole Association

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[99] Davy and Sidgwick, *J. Chem. Soc.*, 1933, 281.

show approximate agreement. This, however, does not settle the question, because any interaction of the solute molecules, whether orientation or aggregation, must affect their activity, and therefore the freezing point of the solution. We can test the question whether polymerization occurs by calculating from the apparent association, as measured by either method, the association constant, *K*, of the reaction:

$$2C_6H_5NO_2 \rightleftharpoons (C_6H_5NO_2)_2$$

$$K = \frac{[(C_6H_5NO_2)_2]}{[C_6H_5NO_2]^2}$$

When we do this we find that *K* is by no means constant; it increases steadily with the concentration, as is shown by the following tabulation, in which *C* is the concentration in moles per liter, and *x* the fraction associated, calculated on the hypothesis that double molecules are formed:

	by freezing point	by polarization	by freezing point	by polarization
0.1	0.049	0.045	0.271	0.247
0.5	0.217	0.186	0.334	0.281
1.0	0.356	0.313	0.429	0.332
1.5	0.470	0.396	0.557	0.362
2.0	0.570	0.460	0.771	0.394

It is therefore evident that the law of mass action cannot be applied to the process. But the condition for the law to be applicable is that the interaction between the molecules should be practically confined to very small distances, as in ordinary chemical reactions. The rapid change in *K* indicates that we are dealing with an effect that is sensible when the molecules are further apart. The fall in activity and in polarization is sufficiently explained by the orientation of the dipoles under the influence of their mutual attractions; in fact the failure of the law of mass action in this case is very similar to that which occurs with strong electrolytes, except that since the force between dipoles varies approximately as the inverse fourth power of the distance, and that between ions as the inverse square, the departure of the "constant" from constancy is less marked with the former.

A comparison of the polarization curves of nitrobenzene in different solvents leads to the surprising conclusion that the association is greater in solvents of higher dielectric constant; the change is not large, but is quite definite:

Solvent	-		
		$C=1.0$	$C=4.0$
Carbon bisulphide[a]	2.63	0.353	0.669
Benzene[b]	2.29	0.313	0.628
Carbon tetrachloride[c]	2.24	0.284	0.629
Hexane[a]	1.88	0.269	0.606

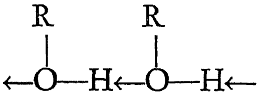
[a] Williams and Ogg, *J. Am. Chem. Soc.*, 50, 98 (1928).
[b] Lange, *Z. Physik*, 33, 169 (1925); Hassel and Uhl, *Z. physik. Chem.*, B8, 199 (1930); Bergmann, Engel and Sandor, *Z. physik. Chem.*, B10, 412 (1930); Pal, *Phil. Mag.*, [7] 10, 265 (1930); Wehrle, *Phys. Rev.*, 37, 1135 (1931).
[c] Pal, *Phil. Mag.*, [7] 10, 265 (1930).

We should expect precisely the opposite order, since on any hypothesis the force between the dipoles must diminish as the dielectric constant of the solvent increases.[99a]

The second type of association, which is found with the alcohols, is shown by Curve *II* in Figure 7. With ethyl alcohol in benzene the curve starts with a value of 72 cc for infinite dilution, rises to 95 cc for a concentration of about 0.3 molar fraction (22 per cent by weight of alcohol, or 4.0 normal), and then falls for the pure alcohol to 52. If we subtract the optical polarization (refractivity) of 20 cc, this gives us an initial polarization of 52 cc, rising to 75 (44 per cent) at the maximum, and falling to 32 for pure alcohol.[100] Substances which give this type of curve differ from those giving the continuous fall of Curve *I* in being associated in the pure state. They also differ in their chemical character; while in nitrobenzene, for example, the oxygen atoms can act as donors of electrons, there is no atom that can act as acceptor, and so association in the ordinary sense is impossible. In an alcohol both kinds of atoms necessary to co-ordination are present, the oxygen as a donor and the hydroxylic hydrogen as an acceptor. The anomalous rise in the polarization curve is accounted for[101] if we suppose that the R—O—H molecules that are present form co-ordinate links with one another:

[99a] It would appear from the recent work of Horst Müller,—*Physik. Z.*, 33, 731 (1932)—that this is due to a small but real difference in the values of the moment in different non-polar solvents.

[100] Errera, *Leipziger Vorträge*, 1929, p. 109.



$$\leftarrow\overset{\overset{\textstyle R}{|}}{O}-H\leftarrow\overset{\overset{\textstyle R}{|}}{O}-H\leftarrow$$

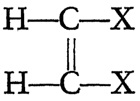
as the concentration increases. The large moments of the co-ordinate links produced account for the rise of the polarization curve. This formation of more complex molecules by co-ordination will not proceed without limit; it will be opposed by the thermal agitation of the molecules; and so at still greater concentrations of the alcohol, the normal orientation of these highly polar polymerized molecules will begin to prevail, and will ultimately cause a fall of the polarization curve.

DIPOLE MOMENTS AND ORGANIC CHEMISTRY

In addition to the general questions raised by the study of dipole moments, their investigation has thrown light on numerous problems, both of structure and of behavior, in organic chemistry.

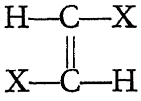
Cis-trans *Isomerism*

The application of dipole moments to molecules of this type is obvious. On the simple principles of the composition of moments a *cis*-disubstitution product of ethylene with identical substituents should be polar, and the *trans* compound non-polar:



$$\begin{array}{c} H-C-X \\ \| \\ H-C-X \end{array}$$

cis



$$\begin{array}{c} H-C-X \\ \| \\ X-C-H \end{array}$$

trans

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[101] Sidgwick, *Z. Elektrochem.*, 34, 450 (1928).

Experiment confirms this conclusion. Errera[102] has measured a series of dihalogen derivatives of ethylene with the following results:

		Cis	*Trans*
Dichloroethylene	$HClC=CClH$	1.85	0
Dibromoethylene	$HBrC=CBrH$	1.35	0
Di-iodoethylene	$HIC=CIH$	0.75	0
Chlorobromoethylene	$HClC=CBrH$	1.55	0
Chloroiodoethylene	$HClC=CIH$	0.57	1.27

The structures given in this table are those previously assigned to the compounds in accordance with the chemical evidence; the dipole moments confirm this except for the chloroiodide, where they lead to the opposite conclusion. Since the moment of C—Cl and C—Br are practically identical, while that of C—I is smaller, we should expect a residual moment in the chloroiodide, but not in the chlorobromide.

This conclusion has been confirmed for the dichloride by the experiments of Debye[103] on X-ray scattering, which showed the distance between the chlorine atoms to be 3.6Å in the *cis* and 4.7Å in the *trans* compound.

The Benzene Problem

The spatial configuration of benzene and its simpler derivatives has now been determined. The X-ray examination of the crystal structure of hexamethyl benzene was carried out in great detail by Mrs. Lonsdale,[104] and showed that the 6 carbon atoms of the ring and the 6 of the attached methyl groups all lie symmetrically in a plane.[105] This conclusion is supported by the general trend of aromatic chemistry, and accounts for the absence of dipole moment in benzene, as well as for the observed impossibility of obtaining optically active substitution-products. If we accept this formula as it stands, we can calculate[106] the moment of a disubstitution product if we know those of the two substituents separately, since the angle between the C—X valences will be 60° in the *ortho*, 120° in the *meta*, and 180° in the *para* position. Hence, if the moment of the link C—X is m, the resultant moment that we should expect a molecule $C_6H_4X_2$ to have is, according to the orientation:

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[102] Errera, *Compt. rend.*, 182, 1623 (1926); *Physik. Z.*, 27, 764 (1926); *Polarisation diélectrique* (Paris, 1928).

[103] Debye, *Physik. Z.*, 31, 142, 419 (1930).

[104] Kathleen Lonsdale, *Proc. Roy. Soc. London*, A123, 494 (1929).

[105] The same is probably true of the 12 atoms in hexachlorobenzene—Lonsdale, *Proc. Roy. Soc. London*, A133, 536 (1931).

[106] J. J. Thomson, *Phil. Mag.*, [6] 46, 497 (1923).

$$\begin{array}{ll} \textit{ortho}: & \sqrt{m^2+m^2+2m^2\cos 60^\circ} = \sqrt{3}\,m \\ \textit{meta}: & \sqrt{m^2+m^2+2m^2\cos 120^\circ} = m \\ \textit{para}: & 0 \end{array}$$

A symmetrical 1,3,5-tri-derivative, $C_6H_3X_3$, would also of course have zero moment. If the two substituents are different, C_6H_4XY, and the moments of C—X and C—Y are m_1 and m_2, we have:

$$\begin{array}{ll} \textit{ortho}: & \sqrt{m_1{}^2+m_2{}^2+m_1m_2} \\ \textit{meta}: & \sqrt{m_1{}^2+m_2{}^2-m_1m_2} \\ \textit{para}: & m_1-m_2 \end{array}$$

If the two moments are oppositely directed with respect to the ring, the same equations apply, the signs being taken into account.

The moments of a large number of di-derivatives of benzene have been measured and compared with the values calculated in this way. It is found that with the *ortho* derivatives the observed moments are always markedly lower—usually 15 to 20 per cent—than the calculated. Attempts have been made to explain this by a spreading of the valence angle, but these are not of much value since it is clear that in substituted benzenes there is an interaction between the substituent dipole and the ring, which certainly affects the moment. For the *meta* compounds the Thomson calculation usually agrees with observation within 10 per cent. The *para* compounds, as we have seen, fall into two classes: those in which the moments of the substituents are symmetrical, which conform to the theory; and those in which they are unsymmetrical, which show a considerable residual moment, due to the flexibility.

The moment of a group C—X is, in general, different according as the carbon is part of an alkyl group, or of an aromatic ring, or of an open-chain unsaturated group. It is to be noticed that in the few instances of the last kind that are known, where the carbon is part of the vinyl group, the moment is practically identical with that of an aryl derivative:

X	Alkyl-X	Aryl-X	Vinyl-X
Alkyl	0	0.4	0.4
Chlorine	1.9	1.7	1.6
Bromine	1.8	1.5	1.5

The differences between corresponding alkyl and aryl derivatives are known for a large number of groups, and have been utilized to throw light on the vexed question of the mechanism by which a substituent in benzene determines the direction of further substitution. This forms part of the more general problem of the way in which one group in an organic molecule affects the reactivity of another, which has been and still is the subject of keen discussion among organic chemists. Detailed theories, similar in many respects, have been put forward by Lapworth, Robinson, Ingold and others. All these theories have this in common, that they ascribe the phenomena to a displacement of the electrons in the molecule. It is obvious that if such displacements really occur, they must be reflected in the dipole moments. The first attempt to test these views from the physical side has recently been made by Sutton,[107] who has been able to obtain support for some of the conclusions of the Lapworth-Robinson theory. He shows that there is a definite relation between the difference of moment of the aryl and alkyl derivatives Ar—X and Alk—X, and the directing power of the substituent X. If we call those moments of which the positive end is remote from the aryl or alkyl group positive, and those in the opposite direction negative, then when *m*(Ar—X) − *m*(Alk—X) is positive, X directs further substitution to the *ortho* and *para* positions; while if this difference is negative, the direction is to the *meta* position. The difference in moment between Aryl—X and Alkyl—X is obviously due to an interaction between the C—X dipole and the rest of the molecule, which is different in the two cases, and clearly greater in the aromatic derivative, owing to the greater susceptibility of the benzene nucleus to modification. One kind of interaction may be assumed in every molecule, a polarization of the electron orbits of neighboring atoms by the C—X dipole; but it is evident from the extent of the differences that a further effect—what the organic chemists have called an electromeric or tautomeric effect—must occur with benzene, and it is the magnitude and direction of this latter which we wish to measure. In order to eliminate the direct polarization as far as possible, Sutton compares the moments of Aryl—X with those of compounds Alkyl—X in which X is attached to a tertiary carbon atom,[108] such as the tertiary butyl derivatives, so that in both the carbon atom of C—X is joined only to carbon.

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[107] L. E. Sutton, *Proc. Roy. Soc. London*, A133, 668 (1931).

TABLE XXXIX

Moments of Aromatic and Aliphatic Derivatives

X	Moment of		
	Ar—X	Alk—X	*m*(Ar—X) − *m*(Alk—X)
CH_3	+0.45	±0.0	+0.45
>O	−1.06	−1.29	+0.23
	+1.55	+1.23	+0.32
Cl	−1.56	−2.15	+0.59
Br	−1.52	−2.21	+0.69
I	−1.27	−2.13	+0.88
CH_2Cl	−1.82	−2.03	+0.21
$CHCl_2$	−2.03	−2.06	±0.0
CCl_3	−2.07	−1.57	−0.50
$CO\cdot CH_3$	−2.97	−2.79	−0.18
CO	−3.04	−2.76	−0.28
$C\equiv N$	−3.89	−3.46	−0.43
NO_2	−3.93	−3.05	−0.88

The results are given in Table XXXIX. The convention is there adopted of calling those moments positive (+) in which the positive end of the dipole is remote from the ring, and those in the opposite direction negative (−).

Of the groups in Table XXXIX, all the first eight, in which the difference is positive, direct further substitution to the *ortho* and the *para* positions; the last four, where it is negative, to the *meta;* while —$CHCl_2$, for which the moments are the same, directs indifferently to all three positions.

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[108] For this reason the values of Alkyl—X in Table XXXIX will be seen to differ slightly from those given earlier in this chapter.

The results show beyond doubt that the directing effect produced by substituents in benzene is due to the consequent drift of electrons in the ring; and the direction of this drift is that required by the Lapworth-Robinson theory.

It is notable that the magnitude of the differences is of the order of one-tenth of that (about 7) which would be caused by the actual migration of an electron from one atom to the next. This might be due either to a complete migration occurring in about 10 per cent of the molecules or to a small shift in each of them; the measurements of the moments give us only their average value. But we can distinguish between these two possibilities and show that the latter represents the facts. On the first hypothesis the drift would affect only a small proportion of the molecules. Now some substituents, such as chlorine, make the rate of further substitution much slower than it is in benzene itself. If they influenced only 10 per cent of the molecules the rate could be diminished by only 10 per cent at the most, since the other 90 per cent would be unaffected and would react as they did before substitution took place. It follows that the electromeric effect must occur in all the molecules of the substance, and must consist in a drift much smaller than that which would be caused by the complete migration of an electron.

It is interesting to compare Sutton's conclusions with the rule for the direction of substitution in benzene which was put forward by Hammick and Illingworth.[109] This rule, which seems to hold in every case, is as follows: If, in a substitution-product of benzene, C_6H_5—X—Y, Y is in a later group of the periodic table than X, or if, being in the same group, Y is of lower atomic weight than X, the direction of subsequent substitution is *meta;* if Y is in an earlier group, or if there is no Y, as in the case of $C_6H_5 \cdot Cl$, then the direction is *ortho-para*. Now we have already seen that if in the link X—Y, Y is from a later periodic group than X, it is the negative end of the dipole, but if from an earlier group it is the positive end; what happens when both atoms come from the same group we do not yet know. Further, in the only examples we have of the replacement of a benzene hydrogen by a single atom, this is a halogen atom, which, coming from a later periodic group than the fourth, is negative to the carbon. Thus there is a direct relation between Hammick and Illingworth's rule and the moment of the substituent group. If we combine these facts with the conclusion given above, that the *ortho-para* directing power involves an electronic drift in the ring away from the substituent, we can distinguish three cases: (1) Y from an earlier group than X (*ortho*, *para*); (2) no Y (*ortho*, *para*); (3) Y from a later group than X (*meta*). The relation between the moment of the substituent and the electronic drift in the ring—indicated by the arrow—in these three is as follows:

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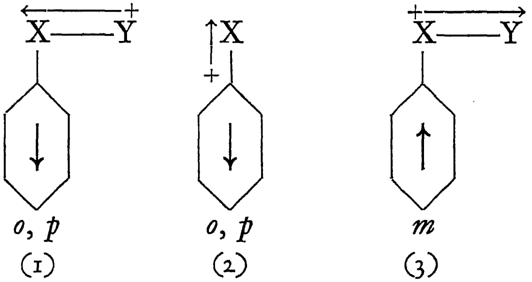
[109] Hammick and Illingworth, *J. Chem. Soc.*, 1930, 2358.



In the first and third the drift is in the same direction as the moment of the substituent, and may be supposed to tend to relieve the strain that this produces;[110] but in the second, where there is only one atom in the substituent group, we have to assume a drift in the opposite direction to the moment, which indicates that some principle is operative which we do not yet understand.

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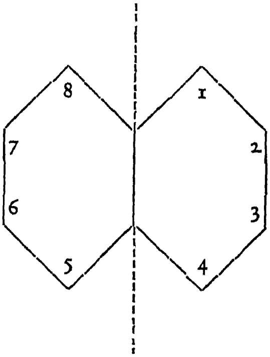
[110] It will be remembered that the ordinary inductive effect of the moment is already allowed for by the comparison with the alkyl derivatives, in which this effect occurs also; the "drift" expresses some further change in the aromatic ring.

Naphthalene

Since in hexamethylbenzene the carbon atoms of the benzene ring lie in the same plane with one another and with the 6 carbon atoms of the methyl groups, we should expect the two 6-rings in naphthalene also to lie in one plane. The earlier investigations of naphthalene led to a different conclusion. The X-ray examination of the crystals was supposed to indicate a zigzag structure. The first measurements of the dipole moment of naphthalene gave a small but definite positive result, which is incompatible with the plane formula. Recently however it has become almost certain that the plane formula is correct. The dipole moment has been remeasured and found to be zero.[111] The moments of a series of derivatives, especially those containing halogens, have also been examined. Now that we know the benzene ring to be plane, we should expect to find that if the two rings in naphthalene do not lie in a single plane, they will be in two planes, inclined at an angle and meeting in the line of the two central carbon atoms, indicated by the dotted line in the figure:



The decisive test of this question is the moment of a 2,6-derivative; this can be non-polar only if the two rings are in one plane. The measurements give for this compound either a zero moment or a very small one, which may be due to experimental error, or to neglect of the atomic polarization, as they were made by the refractivity method. That one ring is plane is shown by the absence of moment in 1,4-dichloronaphthalene; that both rings are plane is at least probable, since 1,5-difluoronaphthalene is non-polar; but both of these compounds could be non-polar even if the planes of the two rings were inclined to one another.

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[111] C. T. Zahn, *Phys. Rev.*, 35, 1047 (1930); J. W. Williams and J. M. Fogelberg, *J. Am. Chem. Soc.*, 53, 2096 (1931).

In general the 1- (α-) derivatives have moments very near those of the corresponding benzene derivatives; the moments of the 2- (β-) compounds are larger. The data are given in Table XL.

TABLE XL

Dipole Moments of Naphthalene Derivatives

1-Fluoronaphthalene	1.42[c,d]		Fluorobenzene	1.45
2-Fluoronaphthalene	1.56[a,d]			
1-Chloronaphthalene	1.59[c]	1.50[d]	Chlorobenzene	1.56
2-Chloronaphthalene	1.72[c]	1.57[d]		
1-Bromonaphthalene	1.58[c]	1.48[d]	Bromobenzene	1.52
2-Bromonaphthalene	1.71[c]	1.69[d]		
1-Iodonaphthalene	1.43[c]		Iodobenzene	1.27
2-Iodonaphthalene	1.56[c]			
1-Nitronaphthalene	3.88[d]		Nitrobenzene	3.93
1,5-Difluoronaphthalene	0[d]			
1,5-Dinitronaphthalene	0.6[f]			
2,6-Dichloronaphthalene	0,[b] 0.60[d,e]			
1,4-Dichloronaphthalene	0[d]			

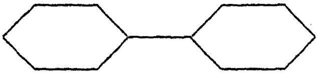
[a] Zahn, *Phys. Rev.*, 35, 1047 (1931).
[b] Williams and Fogelberg, *J. Am. Chem. Soc.*, 53, 2096 (1931).
[c] Parts, *Z. physik. Chem.*, B10, 264 (1930).
[d] Nakata, *Ber.*, 64, 2059 (1931).
[e] Bergmann and Engel, *Z. Elektrochem.*, 37, 563 (1931).
[f] Höjendahl, *Physik. Z.*, 30, 391 (1929).

Diphenyl and Its Derivatives

On account of various chemical peculiarities and of their stereochemical behavior,[112] it was at one time suggested by Kaufler that the two rings in diphenyl do not lie in a plane, as in diagram *I* but are folded over each other, as in *II*. This should obviously be capable of determination by means of the dipole moments. A di-*para*-substituted diphenyl $X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}X$ should, on the plane formula, be non-polar if the X groups are not flexible, while on the Kaufler formula it should be polar. Any doubt whether the groups are flexible can be settled by comparing the compound with the corresponding *para* di-derivative of benzene. If the latter is non-polar, the same groups should give a non-polar diphenyl derivative also, if the plane formula is correct.

---

[112] An excellent summary of the rather complicated history of the chemistry of the diphenyl group is given by Ingold in *Annual Reports . . . of the Chemical Society*, 23, 119 (London, 1926). The interesting stereochemical questions to which they give rise are discussed below in Chapter VI, p. 214.



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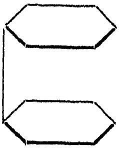

II

The results[113] are given in Table XLI. Earlier measurements indicated that *p*-phenylene diamine was non-polar, but Weissberger and Sängewald[114] showed that the tetra-

TABLE XLI

Moments of p,p′-*Diphenyl Derivatives*, $X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}X$, *and* p-*Di-substituted Benzenes*, $C_6H_4X_2$

X	$X{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}X$	p-$C_6H_4X_2$
H	0	0
F	0	—
Cl	0	0
Br	0	0
NO_2	0	0
CN	0	—
NH_2	1·4	1·5
$N(CH_3)_2$	1·25	1·23
$O{\cdot}CH_3$	1·52	1·74
$O{\cdot}C_2H_5$	1·9	1·74
$O{\cdot}CO{\cdot}CH_3$	1·9	2·2
$CO{\cdot}O{\cdot}CH_3$	2·2	2·2

[113] Williams and Weissberger, *J. Am. Chem. Soc.*, 50, 2332 (1928); *Z. physik. Chem.*, B3, 367 (1929).

[114] Weissberger and Sängewald, *Z. physik. Chem.*, B5, 237 (1929).

methyl derivative had a definite moment, and Williams and Fogelberg[115] re-examined the simple diamine and found that that also was polar.

These results make it clear that the position of the *p,p′*-derivatives of diphenyl is exactly the same as that of the *para* derivatives of benzene; where the moment of the substituent group is symmetrical to the center line of the molecule, the compound is non-polar; otherwise it is polar.

It is therefore evident that the folded structure of Kaufler (page 184, *II*) must be given up, and that the two rings in diphenyl lie in a plane. This is what we should expect, now that we know from the crystal structure of hexamethylbenzene that carbon atoms attached to the benzene ring lie in the same plane with the ring.

Compounds of the Type CA_4

There has been much discussion about the structure of molecules of the CA_4 type, especially penterythritol $C(CH_2OH)_4$ and its derivatives. This was largely due to a mis-interpretation of the physical evidence. Guillemin[116] and Henri[117] suggested on spectroscopic grounds that a molecule CA_4 could have the form of a square pyramid with the carbon at the apex. This conception, though it is opposed to the results of stereochemistry, appeared to be supported by the X-ray examination of the crystal structure of penterythritol, which was thought to indicate that the arrangement of the groups round the central carbon atom could not be tetrahedral.[118] Later work, however, has thrown great doubt both on the spectroscopic conclusions,[119] and on those based on crystal structure.[120]

The dipole moments should enable us to solve the problem. A molecule CA_4 can be non-polar only if it is either plane or tetrahedral, and a plane formula is ruled out on a variety of grounds. A square pyramid, such as Henri advocated, must be polar.

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[115] Williams and Fogelberg, *Physik. Z.*, 31, 363 (1930).

[116] Guillemin, *Ann. Physik*, 81, 173 (1926).

[117] V. Henri. See especially *Chem. Reviews*, 4, 189 (1927).

[118] Mark and Weissenberg, *Z. Physik*, 17, 301 (1923); Huggins and Hendricks, *J. Am. Chem. Soc.*, 48, 164 (1926).

[119] A. E. Ruark and H. C. Urey, *Atoms, Molecules and Quanta* (New York, 1930), p. 436.

[120] Nitta, *Bull. Chem. Soc. Japan*, 1, 62 (1927); Schleede, *Z. anorg. allgem. Chem.*, 168, 313 (1928); *ibidem*, 172, 121 (1928); Möller and Reis, *Z. Krist.*, 68, 385 (1928); Knaggs, *Proc. Roy. Soc. London*, A122, 69 (1929).

The moments for compounds of the formula CA_4 are given in Table XLII.

TABLE XLII

Dipole Moments of Molecules CA_4

A	μ	Ref.
H	0	
Cl	0	
NO_2	0	*a*
CH_2Cl	0	*b*
CH_2Br	0	*a,b,c*
CH_2I	0	*b*
$O{\cdot}CH_3$	0.8	*b*
$O{\cdot}C_2H_5$	1.1	*b*
CH_2OH	ca 2	*c*
$CH_2O{\cdot}CO{\cdot}CH_3$	2.6	*b,c*
$CH_2O{\cdot}NO_2$	2.0	*b*
$CO{\cdot}OCH_3$	2.8	*b*
$CH_2{\cdot}OCH_3$	0.3	*d*
$CO{\cdot}OC_2H_5$	3.0	*b*

a J. W. Williams, *Physik. Z.*, **29**, 683 (1928).
b L. Ebert, R. Eisenschitz and H. von Hartel, *Z. physik. Chem.*, **B1**, 94 (1928).
c J. Estermann, *Leipziger Vorträge*, **1929**, p. 17.
d O. Fuchs, *Z. Physik*, **63**, 824 (1930).

It will be seen that the molecules are always non-polar except where the flexibility of the attached groups will account for the polarity. In penterythritol itself, which was examined by the only possible method, that of the molecular beam (see above page 135), the moment might also be explained as being due to the association of the hydroxyl groups.

A more surprising result is the absence of polarity in penterythritol tetrachloride, tetrabromide and tetraiodide, which has been confirmed for the first two by the beam method. The moment of $-CH_2$-halogen is unsymmetrical, and the corresponding *para* derivative of benzene CH_2Cl– –CH_2Cl has a moment of 1.8, which is obviously due to the rotation of the flexible groups. A symmetrical and non-polar arrangement of the four $-CH_2Cl$ groups round the central carbon is of course possible; but it does not seem probable that the potential of the moments will be strong enough to fix the groups permanently in this position, especially since the C—Cl links are further apart than in ethylene dichloride, which has a considerable moment, and also since the orthocarbonates $C(OAlk)_4$ have moments of about 1.0. It seems more likely that the four groups are held in the position of zero moment partly by steric influences.[121]

Compounds of Divalent Carbon[122]

For the last 40 years it has been assumed, mainly as the result of the work of Nef,[123] that in carbon monoxide, the isocyanides and fulminic acid, the carbon is divalent in the sense that it forms a double link with the next atom thus:

$$\mathrm{C{=}O} \qquad\qquad \mathrm{R{-}N{=}C} \qquad\qquad \mathrm{R{-}O{-}N{=}C}.$$

An alternative formula, in which the carbon shares 6 electrons with the oxygen or the nitrogen, the last pair as a co-ordinate link in which it acts as acceptor, was proposed by Langmuir,[124] and has been adopted by Lewis,[125] Lowry, Sugden,[126] and others. This method of formulation, which may be written in various alternative ways, *e.g.*:

$$\mathrm{O\overset{\rightarrow}{=}C} \qquad\qquad \mathrm{R{-}N\overset{\rightarrow}{=}C} \qquad\qquad \mathrm{R{-}O{-}N\overset{\rightarrow}{=}C}$$

$$\overset{+}{\mathrm{O}}\equiv\overset{-}{\mathrm{C}} \qquad\qquad \mathrm{R}{-}\overset{+}{\mathrm{N}}\equiv\overset{-}{\mathrm{C}} \qquad\qquad \mathrm{R{-}O}{-}\overset{+}{\mathrm{N}}\equiv\overset{-}{\mathrm{C}}$$

$$:\mathrm{O}\,\vdots\,\mathrm{C}: \qquad\qquad \mathrm{R{:}N}\,\vdots\,\mathrm{C} \qquad\qquad \mathrm{R{:}O{:}N}\,\vdots\,\mathrm{C}:$$

has never been definitely accepted, at any rate by organic chemists.

We have seen already that the evidence of the moments is decisively in favor of the Langmuir formulas. The minute moment (0.12) of carbon monoxide can be explained only by supposing that the very unequal sharing of the electrons between the carbon and the oxygen is offset by the transference of an electron from the oxygen to the carbon, and the moment that this hypothesis requires for the $C\equiv O$ link is of the right order (see page 153). In the isocyanides the Nef formula requires that the carbon of the —NC group should be the positive end of the dipole, whereas experiment shows (page 139) that it is the negative end; and here too the value of the moment is exactly that which such a transference would produce (page 168).

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[121] Weissberger and Sängewald, *Physik. Z.*, 30, 792 (1929).

[122] Hammick, New, Sidgwick and Sutton, *J. Chem. Soc.*, 1930, 1876; *Chem. Reviews*, 9, 77 (1931).

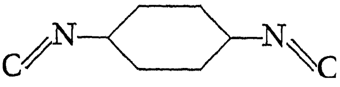
[123] Nef, *Ann.*, 270, 267 (1892); *ibidem*, 287, 265 (1895).

[124] Langmuir, *J. Am. Chem. Soc.*, 41, 1543 (1919).

[125] Lewis, *Valence* (New York, 1923), p. 127.

[126] Sugden, *The Parachor and Valency* (London, 1930), p. 171.

A final proof of the correctness of this view would be to show that the atoms of the $>C-N\overset{\rightarrow}{\equiv}C$ group lie in a straight line, since the Nef formula would involve an angle of about 125° between the single and the double link $C-N=C$, in other words to show that this behaves as a non-flexible group. There is a presumption that this is so, because the moments of *p*-chlorophenyl and *p*-tolyl-isocyanides are so nearly (page 139) the exact difference and the sum, respectively, of those of the single constituents; which indicates that the moment of $-NC$ link, as well as those of the $-Cl$ and $-CH_3$, is symmetrical to the long axis of the molecule. The most conclusive test would be the moment of *p*-di-isocyano-benzene, which on the Nef formula (*I*) should be polar and on the Langmuir formula (*II*) non-polar:



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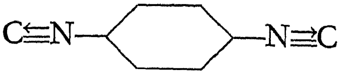


II

This moment has been determined;[127] the substance is very unstable, and decomposes somewhat during the measurements, but the results show that it is non-polar, as formula *II* requires.

These structures are supported by several other lines of evidence: the heats of formation (p. 119); the parachor values;[128] and, for carbon monoxide, by the interatomic distance[129] and the vibrational force constant of the link (p. 123), which is 18.6×10^5, the average value for a triple

[127] Sutton and New, *J. Chem. Soc.*, 1932, 1415.

[128] Hammick, New, Sidgwick and Sutton, *J. Chem. Soc.*, 1930, 1876; Lindemann and Wiegrebe, *Ber.*, 63, 1650 (1930); Sugden, *The Parachor and Valency* (1930), p. 171. The values are:

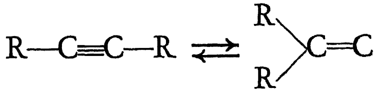
	CO	$-NC$
Calculated: Nef formula,	48.0	40.5
Langmuir formula,	69.6	62.3
Observed:	61.6	65.5

[129] Calculated for $C=O$ 1.24, for $C\equiv O$ 1.14; Observed 1.14Å. *See* Table XX, page 88.

link. They are further supported by the chemical behavior of the isocyanides. It was shown by Nef that they differ from the nitriles in that the unsaturation appears to be confined to the carbon, instead of extending, as it does in the nitriles, to the nitrogen; the addition compounds are of the type $R—N═CX_2$. This results from the nitrogen having already a fully shared octet, while the carbon has a lone pair of electrons. This lone pair also accounts for the readiness with which both carbon monoxide and the isocyanides form co-ordination compounds, such as the carbonyls. Additional evidence is given by the observation that nickel carbonyl is non-polar.[129a] This implies that the link between the carbon and the oxygen is collinear with the co-ordinate link between the carbon—or, less probably, the oxygen—and the nickel; otherwise the free or partially free rotation of the CO groups would lead to a definite moment, as occurs with the methyl and ethyl esters of orthocarbonic acid, which have moments of 2.8 and 3.0 respectively.[129c] But it is only if the CO link is triple that it can be collinear with the single co-ordinate link.

The establishment of these structures removes an apparent anomaly in the behavior of carbon as compared with the other elements of its group in the periodic table. The "inertness" of a pair of valence electrons, changing the valence by two units, is found in many elements of the B subgroups, but is always more marked in the heavier members of any group. In the fourth group this change is very obvious: the inertness is most marked in lead, where the only stable ion is divalent; less in tin, where the stannous ion is unstable; faint in germanium; and practically absent in silicon. It is opposed to all analogy that the divalence should reappear as a relatively stable condition, in carbon.

Nef extended his theory of divalent carbon to other compounds than those we have been considering, and especially to acetylene and its derivatives, which he maintained could exist in tautomeric forms thus:



$$R—C≡C—R \rightleftarrows \begin{matrix} R \\ R \end{matrix}\!\!>C═C$$

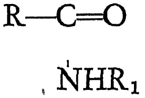
[129a] L. E. Sutton and J. B. Bentley, *Nature*, 130, 314 (1932).
[129c] L. Ebert, R. Eisenschitz and H. von Hartel, *Z. physik. Chem.*, B1, 94 (1928).

This kind of divalent carbon compound cannot be given a co-ordinated structure like that of the isocyanides; the middle carbon atom in the second formula has a fully shared octet and no lone pair, so that it cannot co-ordinate, and the terminal carbon can only have a valence sextet. These views by Nef have been disputed,[130] and are not generally accepted. The band spectrum of acetylene[131a] shows that at least the greater part consists of symmetrical rectilinear molecules. The structure of di-iodoacetylene, to which Nef assigned the unsymmetrical formula, can be determined from the dipole moment: if it is $I—C\equiv C—I$ it must be non-polar, and if it is $I_2C=C$ it should have a considerable moment. The substance has recently been examined[131b] and found to be non-polar.

The existence of the supposed acetal of carbon monoxide, $C(O{\cdot}C_2H_5)_2$,[132] appears from the recent work of Arbusow[133] to be very doubtful.

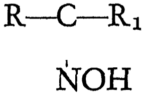
Oximes

The configuration of isomeric oximes has been in dispute for some years; the original view of Hantzsch and Werner was that the two groups that change places in the Beckmann transformation are those that are in on the same side of the C=N group, while Meisenheimer subsequently showed that there were reasons for thinking that they were on opposite sides:

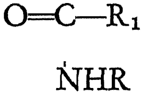


$$\begin{array}{l}\mathrm{R{—}C{=}O}\\ \quad |\\ \quad \mathrm{NHR_1}\end{array}$$

Hantzsch, Werner



$$\begin{array}{l}\mathrm{R{—}C{—}R_1}\\ \qquad |\\ \qquad \mathrm{NOH}\end{array}$$



$$\begin{array}{l}\mathrm{O{=}C{—}R_1}\\ \qquad |\\ \qquad \mathrm{NHR}\end{array}$$

Meisenheimer

The configuration of every pair of isomeric ketoximes is thus interpreted in opposite ways by the two theories, and a similar uncertainty arises about that of the aldoximes as well. It is not easy to find unambiguous chemical reactions that will decide between the two; and although the balance of evidence was, on the whole, on the side of the Meisenheimer theory it was not conclusive.

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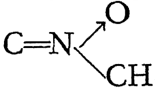
[130] See Biltz, *Ber.*, 46, 143 (1913).
[131a] Mecke, *Z. Physik*, 64, 173 (1930).
[131b] L. E. Sutton and J. B. Bentley. Unpublished.
[132] Scheibler, *Ber.*, 59, 1022 (1926); Scheibler and Adickes, *ibidem*, 60, 272, 554 (1927).
[133] Arbusow, *Ber.*, 64, 698 (1931).

The problem has been attacked by means of the dipole moments, by Taylor and Sutton.[134] The oximes themselves offer difficulties, owing to their association,[135a] and the N-ethers of the oximes of *p*-nitrobenzophenone oxime were examined. The molecule contains two highly polar groups: the nitro group, and the N-ether group  $\mathrm{C{=}N}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{CH_3}\end{smallmatrix}$; the latter, owing to the co-ordinate link, should have a moment of about the same magnitude as that of the nitro group, the oxygen being the negative end of the dipole for both groups. Hence, when the →O is on the same side of the C=N as the nitrophenyl, the two will co-operate and produce a large moment; while when it is on the opposite side they will oppose each other. Two isomeric oximes of *p*-nitrobenzophenone are known, of which one (α) gives, in the Beckmann reaction, *p*-nitrobenzanilide, and the other (β) benzo-*p*-nitranilide (see the formulas below). Each of these oximes can be methylated without conversion into the other, giving the α- and β-N-methyl ethers respectively. The dipole moment of the α ether was found to be 6.60, and that of the β ether 1.09. This makes it certain that in the α ether the co-ordinated oxygen is on the same side as the nitrophenyl group, and in the β ether on the opposite side. Thus we have the relations on page 192. It is therefore evident that in the Beckmann transformation the hydroxyl of the oxime changes places with the hydrocarbon radical on the opposite side of the C=N, as Meisenheimer supposed. A probable mechanism to account for this migration has been suggested by Mills.[135b]

The configurations of the aldoximes cannot be determined in this way, since no isomeric N-ethers of aldoximes are known. Taylor and Sutton in a recent paper[135c] have however established them by comparing the moments of

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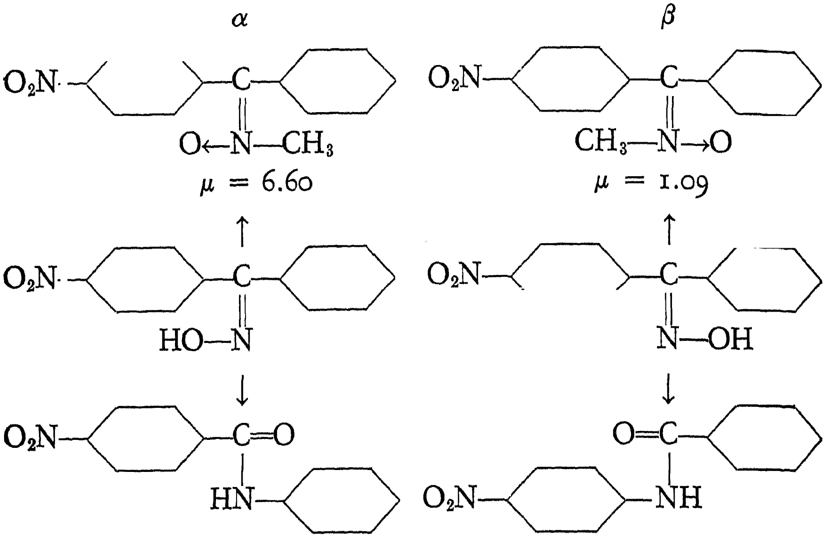
[134] T. W. J. Taylor and L. E. Sutton, *J. Chem. Soc.*, 1931, 2190.

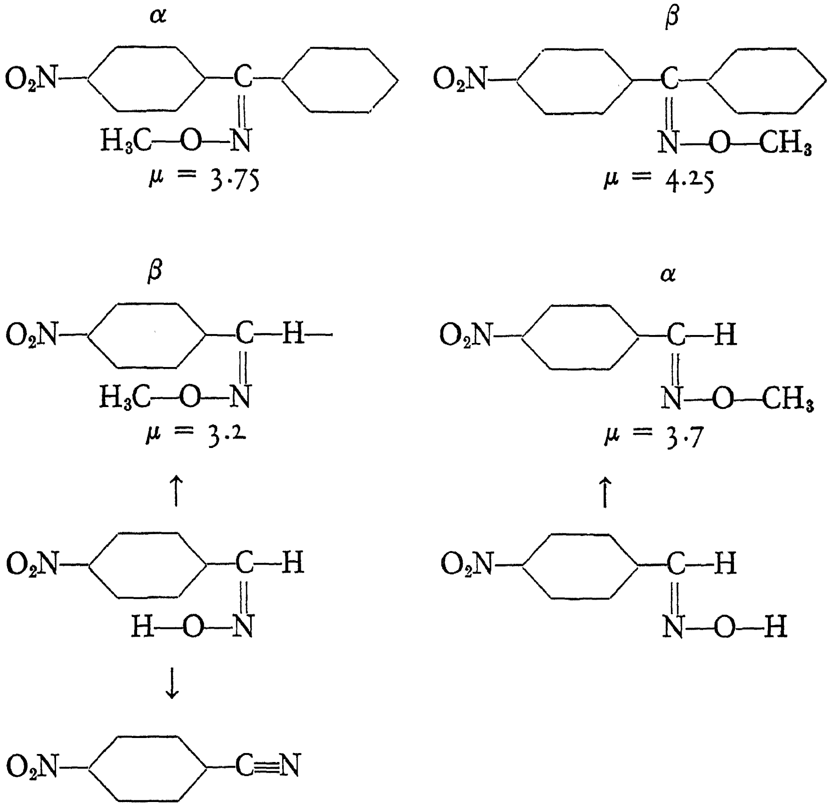
[135a] O. Hassel and E. Naeshagen, *Z. physik. Chem.*, B4, 217 (1929).

[135b] W. H. Mills, in *The Advancement of Science* (London, 1932), page 47. (Presidential address to the chemical section of the British Association for the Advancement of Science, 1932).

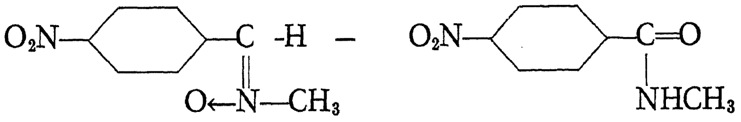
[135c] T. W. J. Taylor and L. E. Sutton, *J. Chem. Soc.*, 1933, 63.



the O-ethers of the two *p*-nitrobenzophenone oximes with those of the corresponding *p*-nitrobenzaldehyde derivatives; in both cases the relations of the O-ethers to their parent oximes are quite unambiguous. The O-ether of the α-ketoxime has a moment of 3.75, that of the β, of 4.25. The difference is naturally less than that between the N-ethers, since the O-ethers do not possess the highly polar co-ordinate link; it is also in the opposite direction, which is likewise to be expected, since the moment of the $\mathrm{N{-}O{-}CH_3}$ group depends on the balance between the opposing moments of the $\overset{+\longrightarrow}{\mathrm{N{-}O}}$ and $\overset{\longleftarrow+}{\mathrm{O{-}C}}$ links, of which the latter must be the larger, as the two atoms belong to more widely separated periodic groups. Of the O-ethers of *p*-nitrobenzaldoxime, the β was found to have a moment of 3.4, and the α of 3.9, the difference being the same as between the ketoxime ethers. It is thus clear that the β-aldoxime ether corresponds to the α-ketoxime ether, and that the β-aldoxime, which is the form yielding the nitrile, has the hydroxyl on the same side of the $\mathrm{C{=}N}$ as the nitrophenyl group.

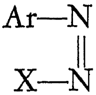
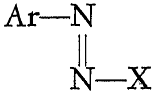


As it was found[134] that the only known N-ether of *p*-nitrobenzaldoxime has a moment of 6.4, this must have the →O on the same side as the nitrophenyl group, and must belong to the β-series. Since this is converted, in the Beckmann reaction, into N-methyl-*p*-nitrobenzamide:



it follows that here also this transformation involves the anti-groups.

Azo Compounds

In his discussion of the structure of the diazo compounds some 30 years ago, Hantzsch pointed out that the —N=N— group was essentially less stable in the *cis* configuration  $\begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{X{-}N}\end{matrix}$ than in the *trans*  $\begin{matrix}\mathrm{Ar{-}N}\\ \|\\ \mathrm{N{-}X}\end{matrix}$ owing to the strain caused by the steric interference, in the *cis* position, of the two attached groups; and that the azo compounds, on account of their surprising stability—azobenzene boils without decomposition at 293°—must belong to the *trans* series.

This conclusion has been confirmed by the measurement of the dipole moment of azobenzene, which is found to be zero.[136] The *p*-monochloro and monobromo derivatives have nearly the same moments (1.55 and 1.42) as chloro- and bromobenzene (1.55 and 1.52).

Azides and Aliphatic Diazo Compounds

These compounds were originally supposed to contain 3-rings; but more recently this view has been abandoned in favor of open-chain structures. The change of opinion was largely due to the work of Angeli, Thiele, and Staudinger, who showed that both classes of compounds could be converted into substances which contain these open chains and which could only be derived from the ring structures if it was supposed that when the ring was opened it broke not at the double link, N=N, but at a single link. This argument is not conclusive, because the double link between nitrogen atoms, unlike that between carbons, is very strong. This is shown by the general behavior of such compounds, and is supported by the observation that the heat of formation (page 120) of the C=N link is at least twice that of the single C—N link, while that of C=C is markedly less than twice that of C—C. Hence we should expect that the same would be true of the link of nitrogen to nitrogen, and that a ring containing two doubly linked nitrogen atoms would break, if at all, not at this double link but at the C—N or the N—N link. The argument from organic chemistry thus leaves the question of structure still open.

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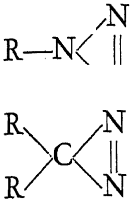
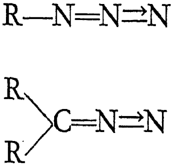
[136] E. Bergmann, L. Engel and S. Sándor, *Ber.*, 63, 2572 (1930).

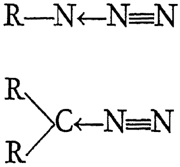
If we assume that the atoms in these compounds have complete octets, they can be formulated in three ways:



I



II

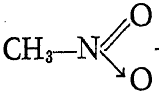


III

Of these formulas, *I* should have a small moment owing to the symmetry of the ring; *II* and *III* both contain co-ordinate links, and so their moments will be large, and they are obviously in different directions.

The volatility both of the azides and of the diazo compounds suggests that their moments are small. A large moment always reduces the volatility, as may be seen from the comparison of the boiling points of the isomeric pairs:

CH_3—O—N=O −12°; $P(OC_2H_5)_3$ 156°; $(CH_3)_2N{\cdot}OCH_3$ 30°



$CH_3{-}N\genfrac{}{}{0pt}{}{=O}{\to O}$ +101°; $C_2H_5(OC_2H_5)_2P{\to}O$ 198°; $(CH_3)_3N{\to}O$ > 180°

where, though the moments have not been measured they may be inferred from the co-ordinate links.[137] If the azides and diazo compounds have ring structures with small moments, their boiling points should lie near those of the corresponding halides which have about the same molecular weights; if they have open-chain structures with large moments the boiling points should lie much higher, nearer to those of the nitro compounds. A comparison of known compounds of these types showed[138] that in boiling-points the azides come near to the corresponding bromides or between them and the iodides, while the diazo compounds come very near the chlorides; the nitro compounds being always much less volatile even than the iodides. This evidence is, therefore, in favor of the ring structures for both classes of compounds.

---

[137] The co-ordinate link of course affects the volatility only through the moment. In a molecule like carbon monoxide, where it diminishes the moment, the volatility is increased. The remarkable resemblances in critical constants between nitrogen, which is non-polar, and carbon monoxide, to which Langmuir drew attention—*J. Am. Chem. Soc.*, 41, 1543 (1919)—are due to the latter being almost non-polar.

[138] Sidgwick, *J. Chem. Soc.*, 1929, 1108.

The values of the parachors both of the azides and of the diazo compounds also support the ring formulas, although the differences to be expected between the two structures are rather small, thus with the azides the calculated value for the ring is 38.6 and for the open chain 44.8; the mean observed value is 40.3.[139]

a. Azides

The dipole moments of the azides have recently been measured, with the following results:

Phenyl azide	1.55[a,b]
p-Tolyl azide	1.96[a]
p-Chlorophenyl azide	0.35[a], 0.47[b]
p-Bromophenyl azide	0.64[a]

[a] Sutton, *Nature*, 128, 638 (1931).
[b] Bergmann and Schütz, *Nature*, 128, 1077 (1931).

This shows that the azide group has a moment of about 1.5, with the negative end remote from the benzene ring. This clearly favors the ring structure. Of the three formulas given above (page 195), *III* is impossible because the moment is in the wrong direction; and it is difficult to understand how a structure like *II*, including a co-ordinate link, can be reconciled with a moment as small as 1.5.

This conclusion, which is supported by such physical evidence as we have about the azides, is the more surprising because the evidence from crystal structures shows clearly[140] that the azide ion $[N_3]^-$ has a rectilinear structure. This admits, on the tetrahedral model, of two formulations:

$[\mathrm{N}\overset{\leftarrow}{=}\mathrm{N}\overset{\rightarrow}{=}\mathrm{N}]^-$ $\qquad$ $[\mathrm{N}\leftarrow\mathrm{N}\equiv\mathrm{N}]^-$

$[\overset{-}{\mathrm{N}}=\overset{+}{\mathrm{N}}=\overset{-}{\mathrm{N}}]^-$ $\qquad$ $[\overset{=}{\mathrm{N}}-\overset{+}{\mathrm{N}}\equiv\mathrm{N}]^-$

IV

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[139] H. Lindemann and H. Thiele, *Ber.*, 61, 1529 (1928); H. Lindemann, A. Wolter and R. Groger, *ibidem*, 63, 702 (1930).

[140] Hendricks and Pauling, *J. Am. Chem. Soc.*, 47, 2904 (1925).

The second of these *V* is obviously improbable, but *IV* should be stable, as it is perfectly symmetrical and has no turning moment. We should expect the N_3 group to have the same structure in the ion as it has in the covalent form. It is to be noticed, however, that the symmetry and non-polarity of the ion, on which its stability may be supposed to depend, cannot be preserved when it becomes covalent; an imaginary phenyl cation can attach itself only to one of the terminal nitrogens, since the central nitrogen has no unshared electrons:

$$[\colon N \vdots N \vdots N \colon]^- + [C_6H_5]^+ \longrightarrow C_6H_5\colon \underset{\cdot}{\dot{N}} \vdots N \vdots N \colon$$

and it will then give, if the open chain is maintained, the molecule $R—N{=}N{\Rightarrow}N$, the second of the three possibilities already mentioned, in which the balance is destroyed by the disappearance of one of the two co-ordination moments. This may explain why the ion and the covalent form have different structures.

b. Aliphatic Diazo Compounds

The moments of some of these compounds have recently been measured,[141] with the following results:

Diphenyl diazomethane	1.42	—
Di-*p*-tolyl diazomethane	1.94	1.90 (calc.)
Di-*p*-chlorophenyl diazomethane	0.62	0.38 (calc.)

These show that the negative end of the dipole is directed towards the nitrogen. The calculated values are derived from the observed moments of toluene and chlorobenzene, on the assumption that the angle between the C—C valences of the methane carbon is 109.5°. The agreement is reasonably good, as no account is taken of the atomic polarization.

Of the three possible structures given above (page 195), only *I*, the ring structure, would be expected to give so small a moment. *III* is definitely excluded,[142] since its moment, besides being too large is in the wrong direction.

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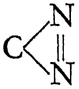
[141] N. V. Sidgwick, L. E. Sutton and W. Thomas. Unpublished.

[142] This is the only formula on which optical activity is possible for the diazo-compounds, but, as will be seen later (page 218), the evidence for such activity is very weak.

II has a dipole in the right direction, but as it contains a co-ordinate link, its moment should be at least four units. The observed moment of 1.4 is larger than we should expect for the group . From the distances C—N = 1.48Å, and N=N = 1.22Å, the angle between the C—N valences must be 48°40′, and hence *m*(C—N=) must be 0.78. But the value of 0.4 assumed above for the moment of C—N is somewhat uncertain and may be too small;[143] also we do not know what may be the effect of the double linkage of the nitrogen on the moment of C—N. Further, the value of 1.4 for the diazo-group is that obtained from the aromatic compounds. The moment of diazomethane and its alkyl derivatives may be expected to differ from this in accordance with Sutton's rule (page 179), and, since the diazo-group is meta-directing, to be smaller.

[143] See D. Ll. Hammick, R. G. A. New and L. E. Sutton, *J. Chem. Soc.*, 1932, 745.

CHAPTER VI.

STEREOCHEMISTRY.

THE last characteristic of covalent links that will be discussed is the angles between two or more links formed by the same atom.

This is the subject of stereochemistry, and the classical method of treatment is through the evidence of organic chemistry, in accordance with the principles laid down by van 't Hoff nearly sixty years ago.[1] In recent times, however, this has been supplemented by evidence derived from the investigation of a whole series of different physical properties, many of which already have been discussed. In this chapter I propose to collect and summarize the results of this convergent series of investigations.

I. EVIDENCE OF ORGANIC CHEMISTRY

The organic evidence stands rather apart from the rest, and may therefore be considered separately. The basis of van 't Hoff's argument is this: If the spatial models of two molecules are superposable, they must represent the same substance. If they are not, the two substances represented must differ in some respects.[2] If the difference between the models, while sufficient to make them non-superposable, is only such that one is superposable on the mirror image of the other, then it follows that both contain the same groups linked through the same atoms, and that the distance from any one atom to any other is the same on both models. The only point in which the two can then differ is in the right- or left-handed arrangement of the groups. The relations between two such isomers may be given in van 't Hoff's own words:[3]

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[1] Van 't Hoff, *Voorstel tot Uitbreiding der Structoor-Formules in de Ruimte* . . . Utrecht, September 1874.

[2] It is, of course, always possible that the two are in continuous tautomeric equilibrium.

[3] Van 't Hoff, *The Arrangement of Atoms in Space* (2d Ed., London, 1898), p. 9.

> All the molecular dimensions being equal in the two forms, we must expect a kind of isomerism distinguished by a near approach to identity. This state of things fully coincides with the facts, and may be summed up as follows.
>
> All physical properties depending on molecular dimensions and attractions (mathematically speaking, on the quantities a and b of van der Waals' theory) are identical in the two isomers: thus specific gravity, critical temperature, maximum tension, boiling point, melting point, latent heat of fusion and vaporisation, etc. The same holds for the physical properties which manifest themselves as the expression of these fundamental quantities on contact with other bodies, *e.g.* solubility.
>
> As regards chemical properties, we must expect exactly equal stability, the same speed of formation and of conversion in given reactions, equilibrium when equal quantities of each are present together, no heat of transformation when one is converted into the other, and accordingly equal heat of formation in both cases.
>
> Finally, the only difference is due to the lack of symmetry, and this is manifested physically in the opposite optical activity, the so-called right- and left-handed rotation, shown by the isomers in the dissolved state—the state, that is, when the rotation must arise from molecular not from crystalline structure.

Two points may be added. It is, of course, obvious that the identity of general physical and chemical properties will no longer hold when the substance with which the isomer is in contact, either as solvent or as reagent, is itself asymmetric.[3a] It also is clear that the phrase "asymmetric atom", which was used by van 't Hoff, is only a convenient abbreviation. When one atom is obviously a center of asymmetry it may be called the asymmetric atom; but whenever this way of speaking leads to difficulties, and there is any doubt which is the asymmetric atom, we have to go back to the real principle, which is that the asymmetry is not that of one atom but of the molecule as a whole. Another point that is sometimes disputed is whether we should describe the van 't Hoff model of the carbon atom as a regular tetrahedron; and it may be pointed out that van 't Hoff's views on this were quite definite. He says,[4] after giving the usual diagrams:

[3a] Professor John R. Johnson has pointed out to me that actually all the evidence up to the present shows that optical enantiomorphs have identical solubilities in chemically inert optically active solvents. For example, *l*-menthyl phthalate has the same solubility in *d*- and in *l*-octanol-2, and the same is true of quinine and of *d*-camphor sulphonic acid. Other experiments are recorded by H. O. Jones, *Proc. Phil. Soc. Cambridge*, 14, 27 (1907).

[4] Van 't Hoff, *op. cit.*, page 8.

> A word as to the shape of the tetrahedra. If we wish to represent only the two possible formulae given above (for $CR_1R_2R_3R_4$), their peculiar lack of symmetry, their object-and-image relation, and the way they may be rendered identical, the regular tetrahedron with variously coloured corners quite suffices. But if the mechanics of the atom is to be taken into account, we must admit, without making any hypothesis as to the nature of the forces acting, that in general these forces will be different between different groups, and the same between similar groups, and then the difference between [the enantiomorphic models] must be expressed in the dimensions also. The edges R_1R_4, R_1R_3, etc., will then be different in the two figures [*i.e.* in both], but the corresponding dimensions in each, R_1R_4 in Fig. 3, R_1R_4 in Fig. 4, will be equal. The two tetrahedra then express by their shape their object-and-image relation (so-called enantiomorphism), and at the same time a mechanical necessity is satisfied.

In other words the tetrahedron formed by joining the centers of the four atoms attached to a carbon atom is regular only when the four attached groups are the same.

The important point, which is implied in van 't Hoff's language and which has been supported by all subsequent experience, is that the four covalences of the carbon atom—and the same applies to any of the covalences of any other atom as well—are all essentially the same. In such a molecule as CA_3B, the relation between C and B is uniquely determined by the nature of the atoms C, B, and A; only one form of such a molecule can exist: there is no difference in the carbon valences such as to make the resulting molecule different according as one special valence is occupied by A or B. There is, of course, a distinction between ionized and covalent links, and among the latter between single, double, and triple links; but the covalent link of any one of these last three species is always of one kind, with properties determined only by the nature of the linked atoms and of any other atoms that may be attached to them. When the four groups are the same, CA_4, the atoms form a regular tetrahedron and the angles between the carbon valences are all equal, except in so far as the four X groups may exert forces on one another that are capable of disturbing this arrangement.

Another point, for which the evidence is purely experimental, may be mentioned here. If we try to synthesize two isomeric substances with formulas so related that one can be converted into the other by changes of single into multiple links and *vice versa*, with changes of valence if necessary, but without either separating two previously united atoms, or joining two that were previously separate, it is always found that only one substance results. The classical example is benzene on the Kekulé formula, but others might be quoted. This does not necessarily prove that the two formulas are not really distinct, but at least it shows that the interconversion of two such closely related structures occurs so easily that under any conditions yet realized they are always in tautomeric equilibrium.

The arguments applied by van 't Hoff to the carbon atom apply of course equally to all other atoms showing tetrahedral symmetry, and with suitable modifications they can be extended to those atoms that have the octahedral type of symmetry discovered by Werner.

I have already discussed elsewhere[5] the evidence for the occurrence of different types of symmetry with various elements, and given the references up to 1927. This need not be repeated in detail here, but before we summarize the results some more recent work should be mentioned.

COPPER

Mills and Gotts had previously shown that 4-covalent copper in its benzoylpyruvic acid derivative gave rise to optical activity, and so must belong to the tetrahedral type. In 1928 Wahl[6] found that 6-covalent copper was of the octahedral type. This work is very remarkable. Wahl showed that when a cupric salt is treated with ethylene diamine, (Ene), it forms a compound $[Cu(Ene)_2(H_2O)_2]X_2$; the tri[ethylenediammino] compound could not be prepared. The tartrate of this di[ethylenediammino] complex was made and resolved, and the active fractions converted into active iodides, so that there is no doubt about the asymmetry. The result is surprising, because in general cupric copper is unwilling to form 6-co-ordinated compounds and readily stops at 4. If the structure of Wahl's compounds rested on analysis alone we should not be sure that the water formed part of the complex cation; but as the chelate ring is symmetrical it is obvious that a cation $Cu(Ene)_2$ would be inactive, and it is only the formation of the 6-co-ordinated complex by means of the two water molecules that makes the activity possible. Further, this complex must be remarkably stable; if the water was even partly dissociated off in solution, the compound would racemize. This instability is unexpected; but there is no doubt that the attachment of chelate groups to an atom may either increase or diminish its power of further co-ordination, although the details of this influence have not yet been worked out. Copper and arsenic are the two elements that have been shown to be tetrahedral when their co-ordination number is 4, and octahedral when it is 6.

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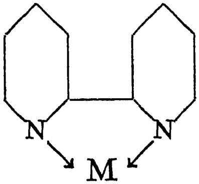
[5] N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford, 1927), Chapter XIII; see also F. M. Jaeger, *Spatial Arrangements of Atomic Systems and Optical Activity*, etc. (New York, 1930), Part I. (George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University, Vol. 7).

[6] Wahl, *Acta Soc. Sci. Fennica*, 14, 1 (1928).

NICKEL

Wahl[6] also obtained and resolved the corresponding nickel tartrate $[Ni(Ene)_2(H_2O)_2]X$; but he gives only scanty data. Recently Morgan and Burstall[7] have prepared complex salts containing co-ordinated α,α′-dipyridyl (Dipyr) molecules; this base forms a chelate ring in the same way as ethylene diamine:



The tris-dipyridyl nickelous salts $[Ni(Dipyr)_3]X_2$ were resolved through the tartrate, and the active tartrate converted into the chloride, which had the very large molecular rotation [M] = 3536°. The active salts were found to be fairly stable in the solid state, but racemized completely in solution in one or two hours at the ordinary temperature. The corresponding tris-dipyridyl ferrous salts were resolved by Werner.[8]

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[7] G. T. Morgan and E. H. Burstall, *J. Chem. Soc.*, 1931, 2213.

The evidence that the 4-covalent nickelous compounds can have a plane structure is discussed below (p. 212).

PLATINUM

Platinum has now been shown to give active 6-covalent complexes. Chernyaev[9] has resolved the salts $[(\mathrm{Ene})(\mathrm{NH_3})\mathrm{Pt}(\mathrm{NO_2})\mathrm{Cl_2}]\mathrm{X}$, $[\mathrm{Ene})(\mathrm{Pyr})\mathrm{Pt}(\mathrm{NO_2})\mathrm{Cl_2}]\mathrm{X}$, and $[(\mathrm{Ene})(\mathrm{NH_3})_2\mathrm{PtCl_2}]\mathrm{X}$. This work is of peculiar interest because platinum is one of the few elements of which there is some reason to think that the 4-covalent compounds are not tetrahedral but plane. Since, further, the co-ordinated compounds of platinum, especially those of co-ordination number 6, are better known than those of any other transitional element, the failure to obtain any active 6-covalent platinum complexes seemed to be related to the peculiar structure of those of the lower co-ordination number. It is now evident that this is not so; whatever may be the structure of the 4-co-ordinated compounds, platinum—like probably all elements that give 6-co-ordination compounds—has the six valences arranged in the octahedral form.

We now come to the small group of elements in whose 4-covalent compounds the four groups appear to lie in the same plane with the central atom. This subject has had a remarkable history in the last few years, and cannot be said to be settled even now. In 1927 it seemed to be established that the plane form of the 4-covalent compounds was given by platinum and by tellurium;[10] to these palladium was subsequently added. As the number and range of the elements that had been shown to have a tetrahedral arrangement of four covalences were increased—there are now more than a dozen—this exceptional behavior of two or three elements became more remarkable. It was then proved that the evidence previously accepted for tellurium is of no value; this element has almost certainly a tetrahedral disposition. The chemical evidence for platinum and palladium has now been seriously challenged. Thus a year or so ago all the indications were that these plane formulas were erroneous. But since then strong evidence has been adduced to show that certain divalent nickel compounds have this plane structure, and Pauling has given reasons based upon wave mechanics for thinking that such an arrangement is possible for a limited number of elements, and especially for the three in question, nickel, palladium and platinum. The elements may be considered in order.

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[8] A. Werner, *Ber.*, 45, 433 (1912).

[9] I. I. Chernyaev, *Ann. inst. Platine*, 6, 23, 40 (1928); see *Chem. Abstracts*, 23, 1581-83 (1929).

[10] The claim of divalent cobalt to be included seems to be very weak.

TELLURIUM

Vernon[11] obtained two isomeric series of compounds of the type of $Te(CH_3)_2I_2$, that gave the same values for the molecular weight. He assumed that they were the *cis* and the *trans* compounds of the plane formula, and their behavior appeared to support this view. The conclusion was attacked by Lowry,[12] who increased our knowledge of these compounds and incidentally showed that the diethyl derivatives behaved in the same way. But he brought no valid arguments against Vernon's view, and had no tenable alternative hypothesis to propose. The overthrow of the theory was due to Drew.[13] He showed that of Vernon's two iodides the α, the first formed, certainly has—apart from steric questions—the formula $Te(CH_3)_2I_2$ which Vernon assigned to it; but that the second form, β, into which this is converted by heating the hydroxide, is not an isomer but a polymer, $Te_2(CH_3)_4I_4$, and is undoubtedly a salt. With alkalies it yields the colorless telluronium hydroxide $Te(CH_3)_3OH$, analogous to the sulphonium hydroxides, and it must be the salt of this base with the constitution $[Te(CH_3)_3][Te(CH_3)I_4]$. This view was confirmed by treating the salt with potassium iodide, when the iodide $[Te(CH_3)_3]I$ crystallizes out, and the potassium salt of the complex anion $K[Te(CH_3)I_4]$ can be obtained from the mother liquor. The mechanism of the conversion of the α-iodide into the β-salt appears to be:

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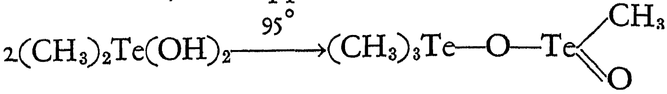
[11] R. H. Vernon, *J. Chem. Soc.*, 117, 86, 889 (1920); I. E. Knaggs and R. H. Vernon, *ibidem*, 119, 105 (1921); R. H. Vernon, *ibidem*, 119, 687 (1921).

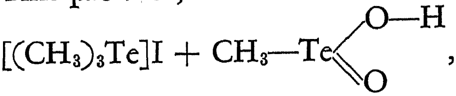
[12] T. M. Lowry, R. R. Goldstein and F. L. Gilbert, *J. Chem. Soc.*, 1928, 307; Lowry and Gilbert, *ibidem*, 1927, 3179; *ibidem*, 1929, 2076, 2867.

[13] H. D. K. Drew, *J. Chem Soc.*, 1929, 560.



$$2(CH_3)_2Te(OH)_2 \xrightarrow{95^\circ} (CH_3)_3Te{-}O{-}Te\begin{matrix} \diagup CH_3 \\ \diagdown\!\!\diagdown O \end{matrix}$$

This product, on treatment with hydriodic acid, gives first



$[(CH_3)_3Te]I + CH_3{-}Te\begin{matrix} \diagup O{-}H \\ \diagdown\!\!\diagdown O \end{matrix}$, and then CH_3TeI_3. These two iodides were isolated, and were found on mixture to give the β-iodide of Vernon.

This shows that the original argument for the plane formula of the di-iodide, which depended on the occurrence of two isomers, is of no value; and so we have no reason to doubt that the 4-covalent derivatives of tellurium, like those of sulphur and selenium, are tetrahedral. The final proof would be the resolution of compounds of this type into optical antimers. This has recently been attempted, apparently with success, by Lowry and Gilbert.[14] They prepared phenyl-*p*-tolyl-methyl telluronium *d*-bromocamphorsulphonate, and showed that the less soluble fraction exhibited mutarotation in acetone. From the acetone solution of this fraction potassium iodide precipitated the corresponding iodide, and this gave a definite rotation in acetone or ethyl acetate, although it racemized very rapidly, the half-life period being only a few minutes. This leaves little doubt that the telluronium ion in question is really optically active, and hence that the arrangement of the three groups about the tellurium atom is tetrahedral, as in the 3-covalent compounds of sulphur. Tellurium must, therefore, be transferred to the class of elements in which covalences of 4 or less are arranged tetrahedrally.

PALLADIUM

Kraus and Brodkorb[15] found that the compounds $(Pyr)_2PdCl_2$, $(C_2H_5NH_2)_2PdCl_2$ and $(NH_3)_2PdCl_2$ all exist in two forms, which they stated were isomeric, since the forms of the first two compounds give the simple molecular weight in phenol solution. Quite recently, however, Drew, Pinkard and Wardlaw[16] have examined these compounds and shown that while one form has the simple formula, the other is bimolecular and is a salt of the type $[Pd(NH_3)_4]$-$[PdCl_4]$. This was proved by a variety of reactions, and especially by preparing mixed salts such as $[Pd(NH_3)_4]$-$[PtCl_6]$, by double decomposition from the second form and K_2PtCl_6. They explain the molecular weights of Kraus and Brodkorb by the ease of transformation of the second form into the first.

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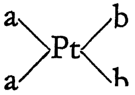
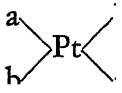
[14] T. M. Lowry and F. L. Gilbert, *J. Chem. Soc.*, 1929, 2867.
[15] F. Kraus and F. Brodkorb, *Z. anorg. allgem. Chem.*, 165, 73 (1927).

PLATINUM

The earlier stages of the controversy about the 4-covalent compounds of platinum may be briefly described.[17] Werner showed that many 4-covalent platinous compounds of the type Pt a_2b_2 occurred in two forms, which he assumed to be the *cis* and the *trans* isomers:





Reihlen measured the molecular weights of the two forms of $(NH_3)_2PtCl_2$ in liquid ammonia, the only solvent in which they would dissolve, and found that while the α gave a simple molecular weight, that of the β form was double. He therefore claimed that they were not isomeric, and that Werner's evidence for the plane configuration was worthless. Grünberg then prepared the two forms of $(NH_3)_2Pt(CNS)_2$, and showed that both gave simple molecular weights. Reihlen replied that these also were not position isomers, but were the normal and the iso-thiocyanates, which obviously was possible. Finally Hantzsch[18] showed that the two isomeric forms of $(Pyr)_2PtCl_2$ were soluble in phenol and gave normal molecular weights therein. This conclusion has not been disputed, and in default of evidence on the other side must be taken to establish a presumption that the 4-covalent platinous compounds—and probably the corresponding palladous compounds—have a plane configuration. At the same time every fresh discovery of an element in which four attached groups are tetrahedrally arranged seemed to make these plane formulas more remarkable; Drew's proof that tellurium must be removed from the list made the position of platinum and palladium still more exceptional, and his reinterpretation of Vernon's data showed how much care is necessary in dealing with these problems.

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[16] H. D. K. Drew, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem. Soc.*, 1932, 1895.

[17] For references see: Sidgwick, *Electronic Theory of Valency* (Oxford, 1927), page 230.

[18] A. Hantzsch, *Ber.*, 59, 2761 (1926).

At this point Angell, Drew and Wardlaw[19] brought forward new evidence about the 4-covalent platinous compounds which, while it does not destroy Werner's hypothesis and Hantzsch's confirmation of it, indicates that further investigation is required. They prepared the two known forms of the thioether addition product, $(Et_2S)_2PtCl_2$. Both isomers are easily soluble in benzene, and were shown to have normal molecular weights in that solvent. The isomerism of the chlorides is repeated in the bromides and the iodides. On keeping, either in the solid state or in solution, or on warming, each form passes over into an equilibrium mixture of the two, in which the α predominates with the bromides, and still more with the iodides.

The striking point is that the α and β forms show differences in behavior which certainly seem too great to be explained by *cis-trans* isomerism. The α compounds are insoluble in water; the β compounds are appreciably soluble and give solutions whose conductivity shows that the compounds are about 50 per cent ionized at $V = 1000$. Their behavior with silver oxide and water is completely different. The α form reacts slowly, the change taking several days, with the liberation of diethyl sulphide and the separation of platinous oxide or hydroxide. The β form reacts rapidly—within 20 minutes—precipitating silver chloride, and leaving in solution the base $(Et_2S)_2Pt(OH)_2$:

$$\alpha:\ Pt(SEt_2)_2Cl_2 + 2AgOH = 2AgCl + 2Et_2S + Pt(OH)_2$$
$$\beta:\ Pt(SEt_2)_2Cl_2 + 2AgOH = 2AgCl + Pt(SEt_2)_2(OH)_2$$

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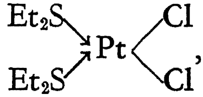
[19] F. G. Angell, H. D. K. Drew and W. Wardlaw, *J. Chem. Soc.*, 1930, 349.

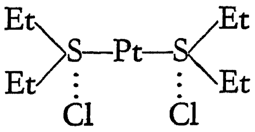
This base, which retains its composition over phosphorus pentoxide, is deliquescent and absorbs carbon dioxide from the air. Conductivity measurements showed that its strength is about equal to that of ammonia (*k* about 1×10^{-5}). With acids it gives a series of salts of the β series that pass over into their α isomers on heating. When treated with defect of hydrochloric acid a proportional amount of the β chloride is formed, showing that the base really has this formula, and is not a complex salt like the β-tellurium base of Vernon.

These properties are enough to show that the two isomers are functionally different, and to make it very improbable that they are *cis* and *trans* isomers. But the assignment of structural formulas offers great difficulties.

For the α series there seems no reason to give up Werner's formulation  $\begin{matrix}Et_2S\\Et_2S\end{matrix}\rightrightarrows Pt\begin{matrix}Cl\\Cl\end{matrix}$, if we make no assumptions as to the spatial distribution. This molecule would be non-ionized, and it might quite well lose diethyl sulphide when the chlorine was replaced by hydroxyl.

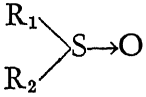
The β compound must then be given some different structure, compatible with the facts that it is partially ionized and that when the chlorine is replaced by hydroxyl it gives a "half-strong base," about as strong as ammonia.

Drew and Wardlaw suggest that it is a sulphonium compound, and that the chlorine has migrated from the platinum to the sulphur. They write the formula:



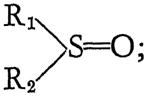
$$\underset{\vdots \atop Cl}{Et_2S}\text{—}Pt\text{—}\underset{\vdots \atop Cl}{SEt_2}$$

where the dotted lines indicate links that can be either ionized or covalent. This suggestion is ingenious, but it is open to serious objections. The first is that experience shows that sulphonium salts are always ionized, and never go over into the covalent form; in the latter the valence group of the sulphur atom would have 10 electrons, two of them unshared, and this does not occur with sulphur; the tetrachloride SCl_4 has been shown by Lowry[20] to exist only in the solid state and then to be probably a salt $[SCl_3]Cl$; the optically active compounds of the type



$$\begin{matrix}R_1 \\ & \rangle S \rightarrow O \\ R_2\end{matrix}$$

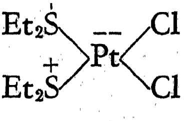
would lose their activity if they were able to go over into



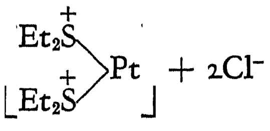
$$\begin{matrix}R_1 \\ & \rangle S = O; \\ R_2\end{matrix}$$

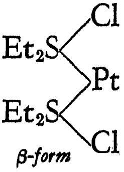
and other examples might be given. The reason of this is that a valence group of more than eight electrons is found only when either: (a) all the electrons are shared; or (b) it can be reduced to an octet or to a fully shared group by counting two of the electrons as "inert," and this inertness does not seem to occur in elements as light as sulphur.[21] Hence, if the β-chloride and its hydroxide are sulphonium compounds they should be strong electrolytes, whereas the conductivity measurements show them to be only partially ionized, and the solubility (and molecular weight) of the β-chloride in benzene shows that it is in the covalent form in that solvent. This objection is not necessarily final, but until an example of a partially dissociated sulphonium compound can be produced it throws great doubt on the formulation.

A second objection is that the ionized form of the β-series as formulated by Drew and Wardlaw is identical with the ion that the α-form would give if its chlorine atoms were ionized; this is obvious if we write the co-ordinated links after Lowry's method:



α-form





β-form

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[20] T. M. Lowry, L. P. McHatton and G. G. Jones, *J. Chem. Soc.*, 1927, 746; T. M. Lowry and G. Jessop, *ibidem*, 1929, 1421; *ibidem*, 1930, 782, 1005; *ibidem*, 1931, 323.

[21] Sidgwick, *Electronic Theory of Valency* (Oxford, 1927), p. 175.

Hence their theory assumes that the two separate compounds are related as the ionized and the unionized states of the same substance. Now no certain instance is known of two separate chemical individuals which differ only in that one has an electrovalent where the other has a covalent link. The transition from one state to the other—which occurs, for example, when we dilute the solution of a weak electrolyte—appears to be invariably instantaneous. Another objection, which is of some force, is that no previous example is known of a 2-covalent platinous compound of the type X—Pt—Y occurring as simple molecules in solution. These objections, like the first, might be overcome, but until parallel examples can be produced the formula suggested for the β-compound must be regarded with suspicion. This does not, of course, affect the validity of the argument that these two forms show differences in physical and chemical behavior too great to be due merely to *cis-trans* isomerism.

On the other hand, even if we agree that the thioether compounds afford no evidence of the plane structure, it does not follow that the evidence of Werner and Hantzsch for the plane structure of the ammine compounds of Werner and Hantzsch loses its value, although it certainly suggests that further investigation of these substances is needed.[22]

One direct piece of evidence strongly in favor of the plane formulas for the 4-covalent platinous and palladous compounds has been pointed out by Lowry.[23] Dickinson[24] concluded from an X-ray examination of a series of salts that in $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$ and $K_2[Hg(CN)_4]$ the four CN groups are arranged tetrahedrally about the central atom of the complex anion; but that $K_2[PdCl_4]$, $(NH_4)_2$-$[PdCl_4]$ and $K_2[PtCl_4]$, which crystallize in a different system—tetragonal and not cubic—have the palladium or the platinum atom lying in the same plane with the four chlorines.

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[22] *See also* H. D. K. Drew, Pinkard, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, 1932, 988, 1004; E. G. Cox, H. Saenger and W. Wardlaw, *ibidem*, 1932, 2216.

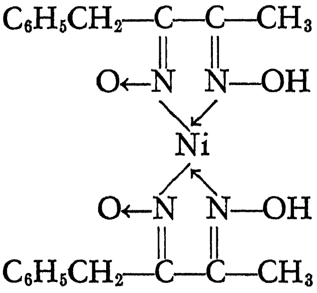
[23] T. M. Lowry, *Nature*, 123, 547 (1929).

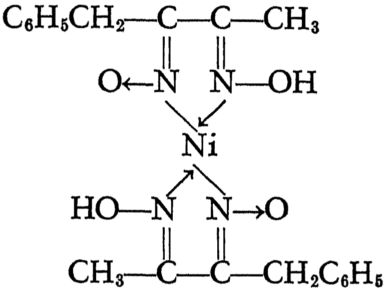
[24] R. G. Dickinson, *J. Am. Chem. Soc.*, 44, 774, 2404 (1922).

Quite recently this conclusion has been confirmed by Cox,[24a] who has shown by X-ray investigation that in tetrammino-platinous chloride $[Pt(NH_3)_4]Cl_2,H_2O$ the four nitrogen ions of the cation lie in the same plane as the platinum, and at the corners of a square. In view of the results obtained by Sugden with the nickel compounds, and of the theoretical conclusions of Pauling, we can scarcely doubt that these elements are capable of forming 4-covalent complexes with a plane configuration.

NICKEL

Sugden[25] has recently produced strong evidence that nickel also is capable of forming 4-covalent compounds of the plane type. He prepared the nickelous derivative of benzyl-methyl-glyoxime, and showed that it occurred in two isomeric forms, α, melting point = 168° and β, melting point = 75–77°, both of which regenerated the original glyoxime on treatment with hydrochloric acid. The formulas are:





It is evident from these formulas that if the two rings are inclined to each other at 90°, as required by a tetrahedral model, isomerism other than stereoisomerism is impossible. The compounds were found to be diamagnetic, as are also the nickel derivatives of dimethyl and diphenyl glyoxime,[26] a fact of particular interest in connection with Pauling's theory discussed below (on page 226).

[24a] E. G. Cox, *J. Chem. Soc.*, 1932, 1912.

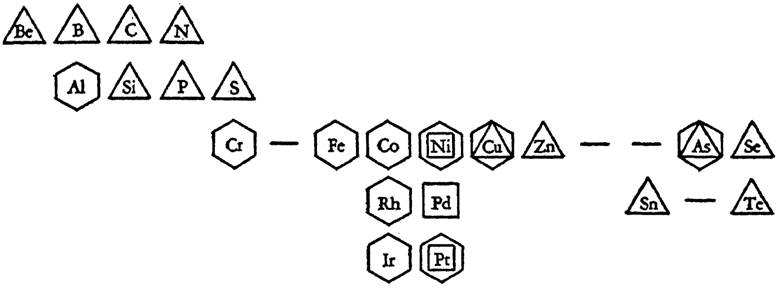
[25] S. Sugden, *J. Chem. Soc.*, 1932, 246.

[26] W. Klemm, H. Jacobi and W. Tilt, *Z. anorg. allgem. Chem.*, 201, 1 (1931); L. Cambi and L. Szegö, *Ber.*, 64, 2591 (1931).

The conclusions arrived at by the stereochemical methods of organic chemistry, for the elements in general are summarized in Table XLIII. The evidence, except in so far as it has been given in this chapter, will be found in the writer's earlier volume.[27]

TABLE XLIII

Stereochemistry and the Periodic Table



△ = Tetrahedral arrangement of 3 or 4 covalences.
□ = Plane ,, of 4 covalences.
⬡ = Octahedral ,, of 6 covalences.

It will be seen that in their 3- and 4-covalent compounds thirteen elements have been shown to have a tetrahedral arrangement, while three—nickel, palladium and platinum—apparently have a plane one. The 6-covalent compounds of ten elements have been examined, and in all of them an octahedral arrangement has been found. From this evidence, which is supported by all the physical evidence discussed later in this chapter, we may conclude that for covalences of 4 and less the tetrahedral form is the rule, although there are perhaps exceptions to it; and that the octahedral form is general for a covalence of 6.

While we are still discussing the organic evidence we may notice certain points of interest that have recently arisen.

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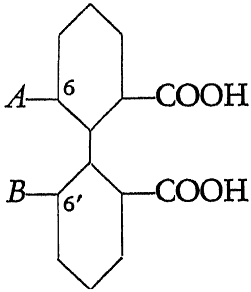
[27] N. V. Sidgwick, *The Electronic Theory of Valency* (London, 1927), Chapter XIII.

The "Obstacle" Theory

A new cause of asymmetry has been detected through the examination of diphenyl derivatives. Christie and Kenner had shown that certain derivatives of diphenic acid in which the 6 and 6′ positions (*A* and *B* in the formula below) were occupied, could be resolved into optical antimers.[28] Further investigation showed that this resolution was always possible if either 6 or 6′ was occupied, usually with NO_2 or Cl; but not if both of these positions were unoccupied, whatever other groups might be introduced. As we have already seen (Chapter V, p. 184), the Kaufler formula, which readily explained the activity, became doubtful on chemical grounds, and was finally displaced in favor of the normal plane formula, through the measurement of the dipole moments. It was therefore necessary to account for the optical activity on the assumption that the line joining the attached carbon atoms of the two rings would pass if produced through the *para* atoms. It was suggested by Bell and Kenyon,[29] and in more detail by Mills,[30] that when both the *ortho* positions on one ring, and one on the other, were occupied by large groups such as CO_2H or NO_2, the rotation of one ring about the median line of the molecule would be prevented, and two enantiomorphic forms would be produced. The consideration of the dimensions of the atoms in question supported



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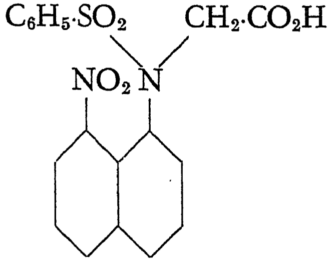
[28] G. H. Christie and J. Kenner, *J. Chem. Soc.*, 121, 614 (1922); *ibidem*, 123, 779 (1923). For further references see Ingold, *Annual Reports . . . of the Chemical Society*, 23, 119 (London, 1926).

[29] F. Bell and J. Kenyon, *Chemistry Industry*, 4, 864 (1926).

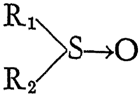
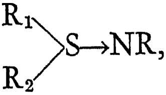
[30] W. H. Mills, *Chemistry Industry*, 4, 884 (1926).

this view. This seemed a very plausible explanation of the activity, and no other could be suggested; but it was obviously desirable to find an analogous behavior in compounds whose structures were better established. This was done by Mills and Elliott.[31] They made the benzenesulphonyl derivative of 8-nitro-1-naphthyl glycine, and resolved it into its active antimers. Here it is clear that the nitro group in the *peri* position interferes with the free rotation of the nitrogen



with its attached groups. The compound racemizes rather readily, the half-period in chloroform at 15° being 17 minutes. The diphenyl compounds are much more stable; and Mills and Elliott point out that, if we assume the benzene rings to be regular hexagons, the distance between the centers of the *peri*-groups in naphthalene is 1.7 times as great as that between the centers at their nearest approach of the 6 and 6′ positions in diphenyl. They also find that the ratio of the velocity constants of racemization of the naphthalene compound at 14.8° and 0.6° is 3.27, which gives the heat of activation of the molecule as 18,500 calories.[32]

Asymmetry due to 3-covalent atoms

The possibility that a trivalent atom in a molecule Xabc might be a center of asymmetry was suggested by van 't Hoff[34] as early as 1878 in his discussion of the stereochemistry of nitrogen, and by Werner[35] for the sulphur atom in the active sulphonium compounds of Pope and Peachey. The occurrence of activity in compounds undoubtedly containing 3-covalent sulphur, of the types  $R_1R_2{>}S{\rightarrow}O$ and  $R_1R_2{>}S{\rightarrow}NR$, was established by Phillips and Kenyon in 1925[36] and has been confirmed by much subsequent work. Recently evidence has been produced that 3-covalent carbon can behave in the same way.

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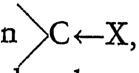
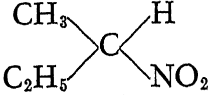
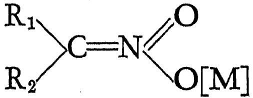
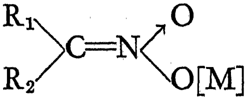
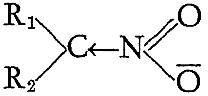
[31] W. H. Mills and K. A. C. Elliott, *J. Chem. Soc.*, 1928, 1291; W. H. Mills and J. G. Breckenridge, *ibidem*, 1928, 2209.

[32] For further work on this subject see: Roger Adams and coworkers, *J. Am. Chem. Soc.*, 52, 2070, 2959, 4098, 4471, 5263 (1930); *ibidem*, 53, 1575, 2353, 2364, 2373, 3453, 3519, 4469 (1931).

[34] Van 't Hoff, *Ansichten Über die Organische Chemie* (Braunschweig, 1878).

[35] A. Werner, *Lehrbuch der Stereochemie* (Jena, 1904), p. 317.

Until lately it seemed that carbon never assumed a covalence of less than 4, except in compounds of unusual instability such as triphenyl methyl; but the recognition that divalent carbon is really 3-covalent, with the structure $C\overset{\leftarrow}{\equiv}X$ (Chapter V, p. 187) suggests that the co-ordinate link with carbon as acceptor, as in  $>C{\leftarrow}X$, which involves a covalence of 3, may occur elsewhere. An instance of this was suggested by Kuhn and Albrecht,[37] as a result of their investigation of the active nitro-paraffins. From the active modification of methyl ethyl carbinol they prepared the active nitro-compound  $(CH_3)(C_2H_5){>}C{<}(H)(NO_2)$ and they showed that this, on treatment with sodium methylate in methyl alcohol, gives a salt that still retains 60 per cent of the activity of the nitro-compound. This salt can be precipitated by ether, and on redissolving in alcohol still has 30 per cent of the original activity. There can be no doubt about the ionization of these salts, and if we accept Hantzsch's formulation of them,  $R_1R_2{>}C{=}N{<}({=}O)(O[M])$ or its modern equivalent  $R_1R_2{>}C{=}N{<}({\rightarrow}O)(O[M])$, they are obviously symmetrical and cannot be active. The only structure that will account for the asymmetry is one in which a co-ordinate link is assumed between the carbon and the nitrogen,  $\begin{matrix}R_1\\R_2\end{matrix}\!>\!C\leftarrow N\!<\!\begin{matrix}O\\\bar{O}\end{matrix}$, and Kuhn and Albrecht therefore propose this formula. Their work has been recently confirmed by Shriner and Young,[38] who prepared the corresponding octane derivative. Starting with the two active forms of octanol-2, C_6H_{13}—CH(OH)—CH_3, they converted them through the bromides into the *dextro* and *levo* nitro-compounds C_6H_{13}—$CH(NO_2)$—CH_3. The *dextro* form, which was the purest, had a rotation of 15.8°. This was converted by the action of sodium ethylate, and also of potassium ethylate, into the salt, and when this salt was treated with hydrochloric acid at $-10°$ the regenerated nitro-compound had about 25 per cent of its original rotatory power. The *levo* form, after conversion into the salt, was treated with acid at $-70°$, and the nitro-compound so formed had 71 per cent of its original activity.

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[36] H. Phillips, *J. Chem. Soc.*, 127, 2552 (1925); P. W. B. Harrison, J. Kenyon and H. Phillips, *ibidem*, 129, 2079 (1926); S. G. Clarke, J. Kenyon and H. Phillips, *ibidem*, 1927, 188.

[37] R. Kuhn and H. Albrecht, *Ber.*, 60, 1297 (1927).

This conclusion has recently been confirmed by W. H. Mills and H. Cole,[38a] who have succeeded for the first time in resolving such an aci-nitro-compound into its antimers. They took phenyl-cyannitro-methane $C_6H_5 \cdot CH(CN)NO_2$ and resolved it through the brucine salt. The sodium salt obtained from this gave a strongly active solution; it retained its activity unchanged at the ordinary temperature, but lost it at once on addition of excess of mineral acid.

There seems no possible doubt about these results, and if they are accepted, Kuhn's formula for the ion, with a co-ordinated 3-covalent carbon atom as the center of asymmetry, affords the only explanation.

A similar structure would seem to be necessary to account for the optical activity of the aliphatic diazo-compounds, if this really exists. Levene,[39] Noyes,[40] and

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[38] R. L. Shriner and J. H. Young, *J. Am. Chem. Soc.*, 52, 3332 (1930).

[38a] W. H. Mills in *The Advancement of Science* (London, 1932), page 41. (Presidential address).

[39] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, 45, 593 (1920); *ibidem*, 52, 485 (1922); *ibidem*, 55, 795 (1923).

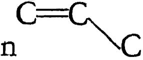
[40] H. M. Chiles and W. A. Noyes, *J. Am. Chem. Soc.*, 44, 1798 (1922); F. E. Kendall and W. A. Noyes, *ibidem*, 48, 2404 (1926).

Lindemann,[41] with their co-workers, found separately that various diazo-esters when prepared from active amino acids retained their optical activity to a small extent ([α] from 1° to 2°). Recently, however, Weissberger and Haase[42] have shown that these results are due to impurities; it was found that when the diazo-compound in the active specimen of diazosuccinic ester is converted by catalytic reduction into succinic ester, the activity remains unchanged, which proves that it must be due to some non-nitrogenous impurity that is not rendered inactive by the reducing agent. More recently, Weissberger and Bach[43] have succeeded in purifying diazosuccinic ester by recrystallization at a low temperature, and have shown that it is then inactive; they have also shown that the active impurity is diethyl *d*-malate, whose boiling point lies very near to that of the diazo-compound.

The evidence adduced by Ray[44] for the activity of the diazo-group in derivatives of camphoric acid is of very doubtful value. A supposed diazo-compound of high activity which he subsequently described[45] he has now found[45] to have a different constitution.

Structure of Benzene

The question of the structure of benzene has already been discussed (p. 176) from the point of view of dipole moments, but there are some further problems on the stereochemical side which deserve consideration.

We know from the crystal structure that in hexamethyl benzene all the twelve carbon atoms lie in a plane. This plane structure for the benzene ring is in complete agreement with its chemical properties. It has long been evident to the organic chemist that the plane formulas of the textbooks represent many of the peculiarities of the aromatic compounds with remarkable accuracy. The refusal of two substituents in the *meta* or *para* positions to join up into a second ring is easily understood if the attached atoms lie in the plane of the ring, but not otherwise.[45a] The plane structure for the ring and its attached atoms is also to be expected from the Kekulé formula if we adopt the tetrahedral model. The angle of the regular hexagon is 120°, and that between the double and single links in  is 125°. Thus the valence angles in benzene are already strained by 5°, and this strain will be increased if the ring is bent out of the plane. Hence, we should expect the ring to be fairly rigid, and the absence of polarity in its simple *para*-disubstitution products, $C_6H_4X_2$, shows that it is so.

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[41] H. Lindemann, A. Wolter and R. Groger, *Ber.*, 63, 702 (1930).

[42] A. Weissberger and R. Haase, *Ber.*, 64, 2896 (1931).

[43] A. Weissberger and H. Bach, *Ber.*, 65, 265 (1932).

[44] F. E. Ray, *J. Am. Chem. Soc.*, 52, 3004 (1930).

[45] F. E. Ray, *J. Am. Chem. Soc.*, 54, 295 (1932); *ibidem*, 54, 4753 (1932).

A more difficult question is whether the six links in the benzene ring are alternately single and double links, as Kekulé supposed, or are six identical links of some intermediate kind. The successful application to benzene of the Thiele theory, in which the difference between alternate single and double links was evened out, combined with the physical interpretation of the covalent link as composed of two shared electrons, led J. J. Thomson and others to the view that the peculiar properties of aromatic compounds are due to the presence in benzene of a peculiar link of three shared electrons. This suggestion, though it is not easy to interpret in the light of the modern wave-mechanical theory of the covalent link,[46] has been rather widely accepted. The dimensions of the aromatic C—C link, so far as they can be determined, are almost the exact mean between those of ordinary single and double links; the distance between the centers of two singly linked carbon atoms is 1.54Å, that between doubly linked atoms—from the crystal structure of unsaturated compounds such as stilbene and from the Swan bands—is 1.33Å the mean of these being 1.44. The distance between the centers of adjacent atoms in an aromatic ring is 1.45 Å from the measurements of naphthalene and anthracene, and 1.42 from Mrs. Lonsdale's results. This is compatible with either view: that this distance is the mean of an equal number of single and double links, or that it is the individual size of a link of an intermediate kind. Mrs. Lonsdale states[46a] that her results are not compatible with the presence in the benzene ring of alternate double and single links; but this objection holds only if those links retain their position during the time required for an X-ray photograph. It has however always been obvious that if we accept the Kekulé formula we must suppose that the two kinds of links change their positions very rapidly, in a much shorter time than is required to observe the positions of the atoms in the crystal, so that on this theory the distance found would be the mean of those of the two kinds of link, as in fact it is.

[45a] It has recently been shown—L. Ruzicka, J. B. Buis and M. Stoll, *Helv. Chim. Acta*, 15, 1220 (1932)—that the junction can be effected if the new ring is large enough; compounds with 16-rings attached in the *meta* and *para* positions to the benzene nucleus were obtained.

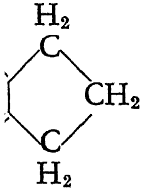
[46] Recently L. Pauling has discussed—*J. Am. Chem. Soc.*, 53, 3225 (1931)—on the basis of wave mechanics, the conditions under which a link of three electrons can occur. He finds that it is possible in NO and NO_2, but definitely concludes that it cannot occur in benzene. For a further discussion of the benzene problem and the "aromatic sextet," from the point of view of quantum mechanics, see E. Hückel, *Z. Physik*, 70, 203 (1931); *ibidem*, 72, 309 (1931); 76, 638 (1932). See also A. Lapworth and R. Robinson, *Nature*, 129, 278; 130, 273 (1932); E. and W. Hückel, *ibidem*, 129, 973 (1932).

Recently, evidence of an organic kind in favor of the Kekulé formula has been brought forward by Mills and Nixon.[47] If we assume that in a doubly bound carbon atom the angle α between the two single bonds is the same as in methane, 109.5°, then the angle β which the single bonds make with the plane of the double bonds will be one-half of $360° - 109.5°$, or 125.25°. The presence of the double link will probably alter these angles to some extent, but we may assume that something like this considerable difference of 16° still remains. In the benzene nucleus, assuming the Kekulé structure and assuming that the hexagon is equilateral—an allowance for the difference in length of the two kinds of links would not appreciably affect the result—a further modification will occur because the internal angle must be 120°. This reduction will no doubt increase the external angles, but here again the effect will not be large and it is clear that the angle α, which each of the external valences makes with the intranuclear single bond on the one side of it, is less than the angle β which it makes with the plane of the double bond on the other side. We may assume these to have the approximate values:

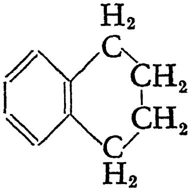
[46a] Mrs. K. Lonsdale, *Proc. Roy. Soc. London*, A123, 494 (1929); *Trans. Faraday Soc.*, 25, 352 (1929).

[47] W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 1930, 2510.

$\alpha = 109^\circ$, $\beta = 125^\circ$. Now the angle of a regular pentagon is 108° and that of a regular hexagon is 120°. We should therefore expect that in a compound, such as hydrindene, in which the benzene ring is fused with a 5-atom ring, the link common to the two rings would be a single bond, while if the fused ring contained 6 atoms, as in tetrahydronaphthalene, the common link would be a double bond, thus:

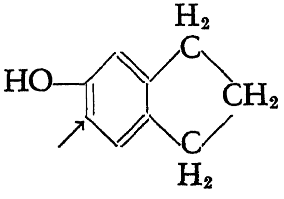


Hydrindene

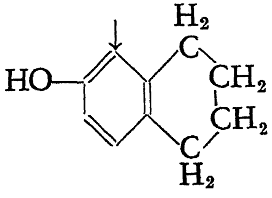


Tetrahydronaphthalene

or at least that these forms would predominate. This conclusion can be tested by the orientation of certain substituents in the hydroxy-derivatives of these substances. We know that the replacement of a hydrogen atom of a phenol, either by coupling with a diazo-compound or by bromination, is closely related to the corresponding reactions of the enols. Now with an enol both diazo-compounds and bromine react in such a way that the substituent becomes attached to the carbon atom that is linked to that bearing the hydroxyl by a double bond. We may conclude that when a phenol undergoes *ortho*-substitution by a diazo-residue or by bromine, the substituent will be attached to that one of the two *ortho*-carbon atoms which is joined to the carbon carrying the hydroxyl by a double bond. Experiment showed that both these reactions follow the course to be expected from the theory. With 5-hydroxyhydrindene both the diazo-group and bromine attach themselves to the carbon marked by the arrow in the following formula,



5-*Hydroxyhydrindene*

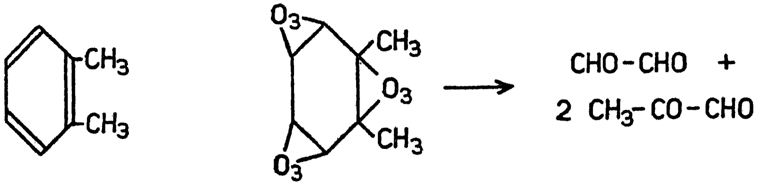


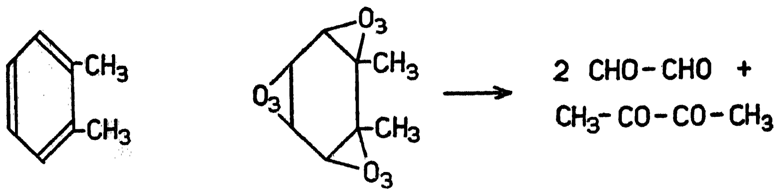
ar-*Tetrahydro-β-naphthol*

that being the one which is doubly linked to the hydroxylic carbon on the Mills theory; while in the corresponding tetrahydronaphthalene compound, *ar*-tetrahydro-β-naphthol, Schroeter[48] has shown that the substituent enters the 1-position, which again agrees with the theory. Bromination of the corresponding acetamido-derivatives gives analogous results.

These facts afford a very strong presumption of the truth of the theory. The only cause, other than stereochemical, for the change in directive influence would be a direct chemical effect on the reactivity due to the replacement of a trimethylene by a tetramethylene group; but these groups are so similar chemically that we cannot suppose that their chemical effects would differ to this extent.

It is obvious that if we are right in assuming alternate single and double links in the benzene nucleus, their positions will shift very readily, and it will only be when the substituents cause a marked difference of stability between the two forms that these positions of the links are fixed; otherwise the behavior of the compound will be in this respect tautomeric. This is illustrated by a recent paper of Levine and Cole,[49] who examined the decomposition products formed when *o*-xylene is treated with ozone. If we accept the usual formulation of this reaction, the two forms of *o*-xylene should give different products, thus:





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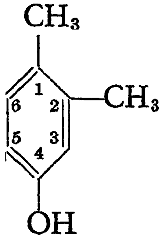
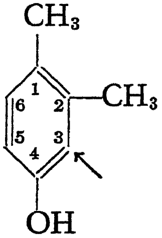
[48] G. Schroeter, *Ann.*, 426, 83 (1922).

[49] A. A. Levine and A. G. Cole, *J. Am. Chem. Soc.*, 54, 338 (1932).

These authors were able to isolate, as such or in the form of derivatives, all the three possible products: glyoxal, methyl glyoxal, and dimethyl glyoxal or diacetyl. Hence it would seem that *o*-xylene occurs in both modifications. Mills and Nixon[47] point out that it has been found that when *as-o*-xylenol couples with diazotized aniline the substituent goes 83 per cent in the 5-position and only 17 per cent in the 3-position,[50] thus:



83 per cent



17 per cent

II. PHYSICAL EVIDENCE

So far we have considered what can be learned about molecular configuration from organic chemistry. As we have seen in the preceding chapters, there have been developed in the last few years a whole series of independent physical methods which throw light on this question. With X-rays and with electron rays we can determine the configuration of molecules in the solid and the vapor state, and measure the distances between their component atoms; from the infra-red spectra—observed either directly, or through the fine structure of the visible and ultra-violet bands—or by means of the Raman effect, or by a combination of these methods, we can discover the number and magnitude of the moments of inertia of the molecule, and hence again the configuration and the interatomic distances; finally, from the electrical dipole moments we can learn much about the nature of the links, and the inclination of the valences to one another. These methods are not more certain than those of organic chemistry, but they are far more widely applicable, the information that they give us is more detailed, and the variety of the methods enables us to check our results. We may now consider the general conclusions which emerge from these investigations.

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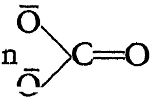
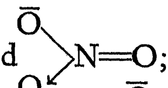
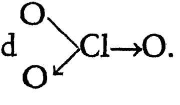
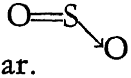
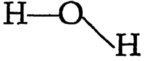
[50] E. Diepolder, *Ber.*, 42, 2916 (1909).

As regards the types of arrangement of the valences of a polyvalent atom, the whole evidence goes to show that with a 4-covalent atom it is almost always tetrahedral, and with a 6-covalent atom it is invariably, so far as we know, octahedral. This, as we have just seen, is the general conclusion reached by the classical methods of stereochemistry. It is also supported by an immense mass of physical data. We may take the 6-covalent compounds first as they offer the simplest problem. The evidence here, apart from that of organic chemistry, is wholly derived from the investigation of crystal structure. This has shown, wherever it has been applied, that in a molecule or ion of the type AB_6 the six B groups are arranged around A at the points of an octahedron. This is found with such diverse types of molecules as the anions XCl_6 and the cations $M(NH_3)_6$ and $M(OH_2)_6$. We have no reason to suppose that any other arrangement occurs.

When we come to atoms with covalences of four or less, we have the converging testimony of a whole series of physical methods, which show that except for a few elements to be considered later, the arrangement is always tetrahedral. Among molecules of the type AB_4, in which the four B atoms are attached by single links, this is established by the crystal structure measurements for a large number of ions MO_4, such as those of the vanadates, perchlorates and permanganates, as well as for such ions as $[Zn(CN)_4]^{--}$ and $[Hg(CN)_4]^{--}$; the dipole moments, the band spectra, and the scattering of X-rays and electron rays by the vapor, all agree in assigning the same structure to the tetrachlorides of elements of the fourth group. When the central atom forms multiple links, the configuration is again that to be expected from van 't Hoff's model. In AB_3, if one of the links is double and the other two single, the molecule is plane, as in  and ; if they are all single, it is pyramidal, as in NH_3 and . In

AB_2, if both links are double ($O{=}C{=}O$, $N\overset{\leftarrow}{-}O\overset{\rightarrow}{-}N$) or if one is triple and the other single ($H{-}C{\equiv}N$, $H{-}C{\equiv}C{-}H$) the molecule is rectilinear; but with a double and a single link, as in  or two single links, as in , it is triangular.

In Table XLIV a series of examples are collected, and the nature of the evidence in each case is indicated: "X-ray"

TABLE XLIV

Molecular Configurations

Molecule	Evidence
Tetrahedral	
CH_4	Spectrum, Moment
CCl_4	Spectrum, X-ray, Electron, Moment
$SiCl_4$	Electron, Moment
$GeCl_4$	Electron
$TiCl_4$	Electron, Moment
$SnCl_4$	Electron, Moment
$[Zn(CN)_4]^{--}$	Crystal structure
$[Cd(CN)_4]^{--}$	Crystal structure
$[Hg(CN)_4]^{--}$	Crystal structure
$[VO_4]^{---}$	Crystal structure
$[ClO_4]^{-}$	Crystal structure
$[MnO_4]^{-}$	Crystal structure
Plane	
$[CO_3]^{--}$	Crystal structure
$[NO_3]^{-}$	Crystal structure
Pyramidal	
NH_3	Spectrum, Moment
PH_3, AsH_3	Moment
PCl_3, $AsCl_3$, $SbCl_3$	Moment
$[ClO_3]^{-}$	Crystal structure
Triangular	
H_2O, H_2S	Spectrum, Moment
SO_2	Spectrum, Moment
Rectilinear	
CO_2, CS_2	Spectrum, X-ray, Electron, Moment
$H{\cdot}C{\equiv}N$	Spectrum
$H{\cdot}C{\equiv}C{\cdot}H$	Spectrum
N_2O	Spectrum, Moment
$[N\overset{\leftarrow}{-}N\overset{\rightarrow}{-}N]^{-}$	Crystal structure

and "electron" refer to the scattering experiments in the vapor, "crystal structure" to the X-ray measurements on the solid, and "moment" to the electrical dipole moments.

The only exceptions among the compounds of 4-covalent elements are those of divalent nickel, palladium and platinum, of which the first and last appear to be plane from the stereochemical evidence, and the last two from that of the crystal structure. This is of particular interest in view of the results of Pauling's recent application of wave mechanics to the problem of stereochemistry.[51] Pauling has developed the method of Heitler and London, which is the interpretation in terms of wave mechanics of Lewis' conception of the covalent link as consisting of a pair of shared electrons. The conclusions at which he arrived are essentially these: The normal arrangement of six covalences is octahedral, and that of four is tetrahedral. But to this latter statement there is an important exception. The linking electrons in a normal 4-covalent atom are those of the first two subgroups of the octet.[52] But in the transitional elements they are drawn, at least in part, from the electronic group next to the outermost group, and this contains electrons of all three subgroups *s*, *p*, and *d*. If the linking electrons occupy *d* levels, Pauling finds that a plane configuration with the four valences at right angles is possible. The compounds of divalent nickel, palladium and platinum are precisely those in which we should expect this arrangement to occur. A further point follows from the theory, which gives us a way of testing the conclusion experimentally. The electrons of the *d* levels are concerned in producing the magnetic moment of the atom, but they cannot do this when they are acting as shared electrons. The formation of this plane configuration will therefore involve a definite decrease of the (*para*) magnetic moment: in nickel this will become zero. As we have seen, Sugden has tested the magnetism of his nickel compounds and found them to be diamagnetic, which is a strong confirmation of the truth of the theory.

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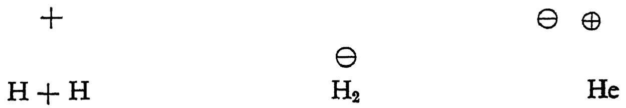
[51] L. Pauling, *J. Am. Chem. Soc.*, 53, 1367 (1931).

[52] It will be remembered that the electrons of an octet are divided into two subgroups of 2 and 6; those of an 18 group into three subgroups of 2, 6, and 10. The values of the second quantum numbers for these subgroups are $k = 1,2,3$ or $l = 0, 1, 2$. The spectroscopic designations of the three are *s*, *p*, and *d*, respectively.

A further conclusion of Pauling's for normal atoms is that while for a covalence of four the arrangement in AB_4 is that of a regular tetrahedron with valence angles of 109.5°, this is modified when the covalence is reduced to three or two, and the angles then become 90°. The quantitative determination of valence angles has not yet been sufficiently developed to enable us to test this conclusion experimentally.

On the theoretical side the details of Pauling's theory should be received with a certain reserve, pending further confirmation. Wave mechanics gives us the complete equations for a single atom, but in order to get at those for a molecule, that is to attack the problem of covalence, we have to proceed by approximation. The method of doing so was pointed out by Hund,[53] who showed that we can regard a molecule as an intermediate stage in passing from two atoms to a single atom having the same number of positive and negative charges; for example, the hydrogen molecule is intermediate between two separate hydrogen atoms and a helium atom, thus:



We can therefore approach the problem of the molecule from two sides: either from that of the two separate atoms, or from that of the single atom produced by their coalescence. Heitler and London adopted and developed the former method, from the two atoms, Pauling has developed it still further. Hund[54] has recently been approaching the problem from the other side, by considering the effect of a division of the nucleus. With either method the process is the same: to begin by considering small changes and calculating the perturbations thereby produced, and then to extrapolate the results for the distance between the nuclei in the molecule. It is obvious that if they are correctly applied the two methods must agree, and either must give the correct result. The difficulty is that the calculations of the perturbations involves approximations, and the extrapolation is rather large. Where the two methods, starting at either end, give the same result, we may accept it as true; but if they disagree, either or both may be wrong and further investigation is required.

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[53] F. Hund, *Z. Elektrochem.*, 34, 437 (1928).

[54] Hund, *Z. Physik*, 73, 1, 565 (1931); 74, 429 (1932).

On the general question of the existence of a resonance effect between two atoms which is the basis of Heitler's and London's theory of the covalent link, the two methods agree, and there is no reason for doubt. The resulting idea of two electrons from the two atoms forming a link by virtue of this effect, that is, of the Lewis mechanism of covalence, follows directly and is equally beyond doubt. But when we come to the directions of the several valences, that is, to the stereochemical questions that we are now considering, the position is not so certain. Pauling's conclusions undoubtedly follow from the method of Heitler and London; but Hund has shown that if we start from the other end, with the big atom, any value can be obtained for the valence angle from 0° to 180°. This does not prove that Pauling's conclusions are wrong—the error may lie in Hund's calculations—but it does show that they should be accepted with reserve until further work has detected where the error in the one or the other of the methods lies. Meanwhile any confirmation from the experimental side, such as that which Sugden's nickel compounds have provided, is of great value.

All the atoms considered so far have contained at least an octet of valence electrons. There does not seem to be any reason to assume that the same valence angles must occur with an atom which has less than eight valence electrons; but our knowledge of the stereochemistry of such atoms is very scanty.

With the co-ordinated hydrogen atom we have no evidence at all as to the size of the valence angle, unless it may be said that the ready replacement of such an atom in chelate compounds, for example in the β-diketones, by atoms of heavy metals suggests that this causes no great difference in the strain, and that therefore the valence angle of the hydrogen must be large—say 180°—to make up for the difference of diameter. This argument, however, is of little value; it is true that the diameter of the ordinary 1-covalent hydrogen atom is 0.75Å and those of many of the metals which replace it from 3 to 4 Å, but if the co-ordinated hydrogen atom really has four shared electrons—a view which the quantum physicists have not yet accepted—its diameter may be expected to be thereby increased; the diameter of the negative hydrogen ion, H^-, is 2.7Å.

For other elements the evidence is at present slight, largely on account of the properties of the compounds which might be expected to supply it. These are necessarily confined almost entirely to the covalent compounds of elements in the second and third periodic groups. Further, the crystal structure of, for example, the halides and the oxides of these elements are of little value from this point of view, owing to the great probability that in these compounds the valence octet is completed by co-ordination. The volatile compounds of this type are usually unstable, and have been but little investigated. The few relevant facts which are known all appear to be compatible with the view that when the octet is incomplete, three valences lie in a plane and two in a straight line. The dipole moment of boron trichloride was found to be zero in benzene,[55] and 0.21 (which may be taken to mean that it is non-polar) in carbon tetrachloride.[56] If the molecule were pyramidal, with a tetrahedral angle of 109.5°, its moment would be equal to that of a single B—Cl link; on the Pauling theory of a right angle it would be somewhat larger. As we have seen, the moment of a link is usually greater the further apart are the periodic groups from which the atoms come, so that we should expect a pyramidal BCl_3 molecule to have a moment greater than that of the C—Cl link, which is 1.7. The practically complete absence of moment suggests that the BCl_3 molecule is plane. Again, the moment of mercury diphenyl and, which is more conclusive, that of mercury di-*p*-chlorophenyl, have been found[57] to be less than 0.4, which indicates that the two valences of the mercury are in one straight line.

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[55] H. Ulich and W. Nespital, *Z. Elektrochem.*, 37, 559 (1931). They also found beryllium chloride and bromide to be non-polar, but, as they admit, the solutions were too dilute for the results to be of value.

[56] E. Bergman and L. Engel, *Physik. Z.*, 32, 507 (1931).

The crystal structure of dimethyl thallium iodide, $[(CH_3)_2Tl]I$ has been examined by Powell,[58] and the results indicate that the C—Tl—C atoms lie in a straight line. The nature of this compound, and the great stability of the dialkyl thallium radical, which is like that of the mercury dialkyls, make it unlikely that the valence group of the thallium is completed by co-ordination.

Thus the evidence, so far as it goes, suggests a plane structure for the 3-covalent and a rectilinear for the 2-covalent compounds of atoms with "incomplete octets."

Having seen what conclusions can be reached as to the general types of configuration of the molecules formed by various kinds of atoms, the next point is to consider how far these types can be modified by the particular conditions of the molecule, and how far the relative positions and distances of the atoms in a molecule are rigidly determined. We may distinguish modifying influences of four different kinds.

We first have the possibility of the rotation of atoms with their attached groups round the line of a single link, which leads to the existence of flexible molecules, already discussed in Chapter V (page 156). This rotation involves no change either of the valence angles or of the interatomic distances; its extent is determined by the opposing influences of the attraction or repulsion of the dipoles, and the thermal agitation. At the ordinary temperature the distance at which the dipole attraction is equal to the thermal effect is 1Å for two very small moments of 0.2, as in C—H; it is 3Å for average moments of 1.0; and 7Å for exceptionally large moments of 4.0. Practically, this means that the rotation will be restrained and the position determined by two dipoles of average moment if they are separated by less than the diameter of two atoms (other than hydrogen), but that the rotation will be free and all possible positions equally favored if the distance is much greater than this. The influence of this factor is of special importance when we are considering the relation between the shape of an organic molecule and its reactivity.

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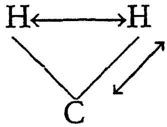
[57] L. E. Sutton and G. C. Hampson, unpublished results.

[58] H. M. Powell and Miss D. H. Crowfoot, *Nature*, 130, 131 (1932).

The second possible modification is that of the interatomic distances. Here, as we saw in Chapter III, the variations are much smaller than has been generally recognized. The change of state from solid to gas has little effect;[59] as we pass from single to double and triple links we find a steady contraction, but this we can allow for; and if we do so, we can get values of the effective atomic radii which will enable us to calculate the interatomic distances in covalent molecules with an error that seldom exceeds 0.1Å.

The third modification is that of the valence angles. This is less easy to determine, and so our data are far less numerous than for the distances. There is however, definite evidence that the angles are more subject to variation than the distances. This is shown clearly by the Raman spectra.[60] With a polyatomic molecule we get Raman lines due to the vibration of atoms in the line of the valence, which gives us the restoring force for change of length of the link—the "stretching constant"—and others due to changes in the distance between two atoms linked to a common atom but not to each other, *i.e.* to changes in the valence angle—the "bending constant." Thus a series of alkyl derivatives all give two lines obviously depending on the oscillations of the CH_2 groups; one of these has a frequency of about 3000 cm^{-1}, and must be due to the stretching of the link, since it occurs whenever the molecule has a C—H group; the other line, with a frequency of about 1400 cm^{-1}, must be due to the bending of the C—H valences, since it is found only when the molecule has CH_2 groups:



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[59] In solid salts the ionic attraction may in extreme cases considerably lengthen a covalent link. The N—O distance in the nitrate ion is found to be 1.15 Å in sodium nitrate and 1.40 Å in lithium nitrate, owing to the stronger attraction of the smaller ion. This is what Goldschmidt has called "contrapolarization."

[60] See D. H. Andrews, *J. Ind. Eng. Chem.*, 23, 1237 (1931).

Since the masses of the atoms concerned in both of these are the same the restoring force is proportional to the square of the frequency, so that for the C—H link the force which resists stretching is greater than that which resists bending, in the ratio $3000^2/1400^2 = 4.6$.

From the spectral data we can calculate the average displacement which such a hydrogen atom would suffer on collision with another molecule, if the collision took place (1) in the direction of the link, and (2) across it. For (1) involving a compression of the link, the force constant, f, for C—H is 4.6×10^5 dynes per centimeter. For (2): the bending, it is 1.0 in the same units. At 25° the thermal energy of a molecule is 4.08×10^{-14} ergs. If we call the distance through which the hydrogen atom is moved on collision x, the force which the colliding molecule exerts is $4.08 \times 10^{-14}/x$ and this must be equal to $f \times x$. Hence:

$$\frac{4.08 \times 10^{-14}}{x} = fx, \text{ or } x^2 = \frac{4.08 \times 10^{-14}}{f}$$

hence: for stretching constant 4.6×10^5, $x = 0.030$ Å, and for bending constant 1.0×10^5, $x = 0.064$ Å. This is, of course, calculated on the incorrect assumption that the transfer of energy is continuous. As a fact it can only occur in quanta; and the first vibrational stretching quantum corresponds to a half-amplitude of 0.08 Å. Thus at 25° only a small proportion of the collisions will lead to this amount of compression. Since the deformation is proportional to the square root of the thermal energy, it follows that the temperature at which the average molecule will have enough thermal energy to communicate one quantum of vibrational energy to the hydrogen atom will be $(0.08/0.03)^2 \times 300°\text{Abs} = 1860°\text{C}$.

Another cause of modification of the valence angles is the mutual repulsion of atoms that are not linked, which occurs whether they are in different molecules or in different parts of the same molecule. The interatomic distances we have considered in Chapter III are those between linked atoms; when the atoms are not linked, the distances are much greater. In the crystalline state there is abundant evidence that we can only account for the whole space occupied by the molecule if, after we have built up the molecular model by means of the "internal" radii deduced from the lengths of the links, we put round it an outer layer or envelope, which is not much less than one ångström thick. For example, in solid benzene hexachloride[61] the minimum distance between the nuclei of two chlorine atoms belonging to different molecules is 3.74 Å. This gives an external radius for chlorine of 1.87, and if we subtract the internal radius of 0.97, we are left with an envelope 0.90 Å thick. So too Hendricks has shown[62] that in a whole series of solid organic compounds the nearest approach of two carbon atoms of different molecules is between 3.6 Å and 3.9 Å, the internal diameter of carbon being 1.54 and that of hydrogen 0.75 Å. In graphite the distance between the separate flat sheets, each of which is really a giant molecule, is 3.41 Å. These distances are due essentially to the electrostatic repulsions of the electrons, whose magnetic moments are already paired within the molecule. This force will gradually increase as the atoms approach one another, until it balances the van der Waals attraction, which is due to polarization and resonance.

In the gaseous or liquid state we should expect the distances to be smaller, since the molecules have greater freedom of motion. Accordingly we find that the "collision radii", calculated from the viscosities of gases, indicate an envelope—an excess of the radius so calculated over its value in a link—of the order of half an ångström. The most striking evidence is that of the distances between the chlorine atoms in the chlorination products of methane, as measured by the scattering of X-rays by the vapor.[63] The results show that the Cl—Cl increases from 2.99 ± 0.03Å in carbon tetrachloride to 3.23 ± 0.1 in methylene chloride. It follows that in the latter the atomic repulsion is sufficient to separate the chlorine atoms, against the resistance which the valences offer to bending, to a distance of 3.2 Å, which involves an external radius of 1.6 or an envelope of 0.6 Å. This is an example of that tendency of two large atoms or groups attached to a central atom to separate as the other groups on the same atom become smaller, which is commonly known as the Thorpe-Ingold effect; and though the quantitative form which Ingold gave to it cannot be maintained, there is no doubt that qualitatively the effect is a real one.[64] It is evident that the cause is to be found in the mutual repulsion of the atoms.

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[62] S. B. Hendricks, *Chem. Reviews*, 1930, No. 4.
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